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Olefin Hydroarylation Catalyzed by a Single-Component Cobalt(-I) Complex

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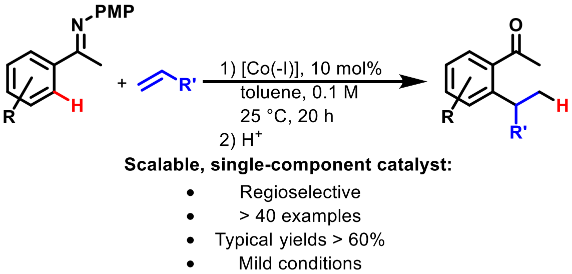
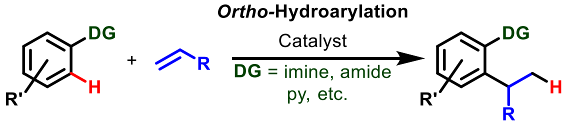
ABSTRACT: A single-component Co(-I) catalyst, $[(PPh_3)_3Co(N_2)]Li(THF)_3$, has been developed for olefin hydroarylations with (*N*-aryl)imine substrates. More than 40 examples were examined under mild reaction conditions to afford the desired alkyl-arene product in good to excellent yields. Catalysis occurs in a regioselective manner to afford exclusively branched products with styrene-derived substrates or linear products for aliphatic olefins. Electron-withdrawing functional groups (e.g., -F, $-CF_3$, and $-CO_2Me$) were tolerated under the reaction conditions.



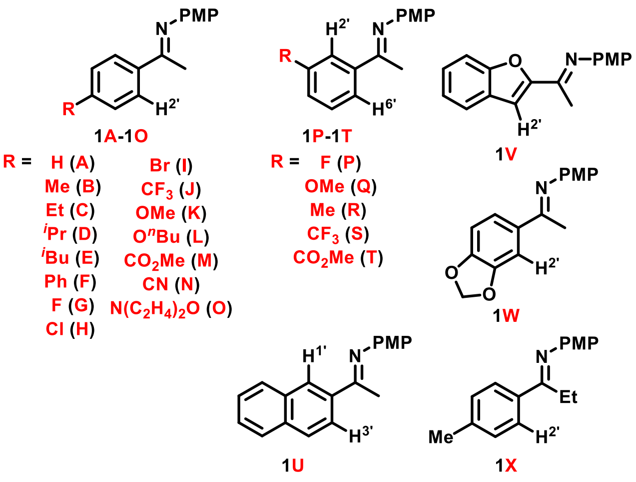
Recent developments in metal-mediated C−H bond activation chemistry have enabled new catalytic transformations to generate value-added products.[1−4] Late-stage C−H functionalizations present attractive alternatives to molecular elaboration methods such as cross-coupling, which require sacrificial, costly, and often toxic reagents. In particular, olefin and alkyne hydroarylations have provided atom-economical routes for formation of C−C bonds.[5−7] The Murai group[7,8] described the first hydroarylation precatalyst, $RuH_2(CO)(PPh_3)_3$, and subsequent developments involving heavier, late-transition metal catalysts (i.e., with Rh,[9−14] Ir,[15−21] Pd,[22−26] and Pt[27−31]) illustrated the synthetic value of hydroarylation as a convenient transformation for C−H bond diversification. However, given the low abundance and high cost of such metals,[32] it is important to develop efficient catalysts based on environmentally benign first-row metals. Indeed, recent advances toward this goal highlight Ni[33−35] and Co[4,36−49] catalysts as suitable alternatives.



(1)

Cobalt catalysts have emerged as a versatile platform for *ortho*-directed C−H bond derivatization (eq 1).[4,36−49] Current Co-catalyzed *ortho* hydroarylations typically require *in situ* catalyst generation, whereby CoX_2 salts are treated with an excess of nonstandard Grignard (e.g., Me_3CCH_2MgBr or Me_3SiCH_2MgBr) and triaryl phosphine [e.g., $P(3\text{-}Cl\text{-}C_6H_4)_3$] additives.[41−48] For these complex catalytic mixtures, the nature of the active species and its mode of action are not well understood; moreover, the addition of excess reactive, nucleophilic co-reagents limits the functional group tolerance.

Scheme 1. Imine Coupling Partners 1A−1X[a]



[a]The catalytically cleavable C−H bonds are labeled with 1′, 2′, 3′, or 6′.

Studies in this laboratory on the mechanism of alkyne hydroarylations catalyzed by cobalt led to identification of a well-defined Co(-I) complex, $[(PPh_3)_3Co(N_2)]Li(THF)_3$ (**Co-Li**), as a single-component hydroarylation catalyst with

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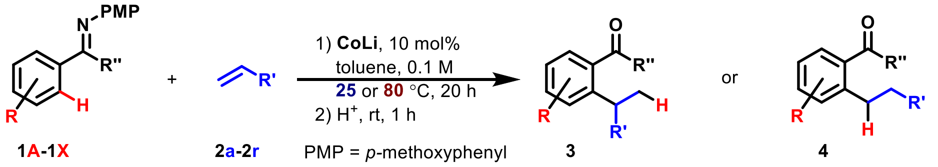
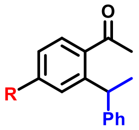
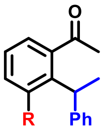
Scheme 2. Olefin Hydroarylations with (*N*-Aryl)aryl Imines Catalyzed by Co-Li[a,b]



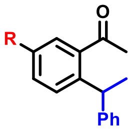
1A-1X **2a-2r** PMP = *p*-methoxyphenyl **3** **4**



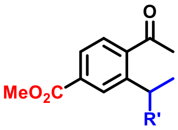
Prod.	R	Yield 25 °C (%)	Yield 80 °C (%)
3Aa	H	83	53 (39)
3Ba	Me	62	46 (35)
3Ca	Et	81	39 (26)
3Da	^{i}Pr	72 (55)	29
3Ea	^{i}Bu	74 (54)	24
3Fa	Ph	77	83 (66)
3Ga	F	89	72 (55)
3Ha	Cl	40	16 (10)
3Ia	Br	0	0
3Ja	CF_3	50	92 (69)
3Ka	OMe	83	66 (56)
3La	O^nBu	51 (46)	16
3Ma	CO_2Me	quant	92 (77)
3Na	CN	0	12 (8)
3Oa	$N(C_2H_4)_2O$	19 (12)	7



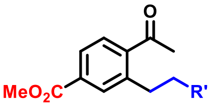
Prod.	R	Yield 25 °C (%)	Yield 80 °C (%)
3Pa	F	89 [20][c] (67)	38
3Qa	OMe	7	3



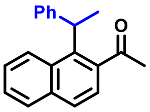
Prod.	R	Yield 25 °C (%)	Yield 80 °C (%)
3Ra	Me	30 (13)	10
3Sa	CF_3	36 (14)	33
3Ta	CO_2Me	97 (91)	65



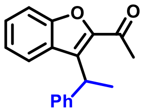
Prod.	R'	Yield 25 °C (%)	Yield 80 °C (%)
3Ma	Ph	quant	92 (77)
3Mb	2-(Me)C_6H_4	33 (31)	-
3Mc	4-(Me)C_6H_4	quant (95)	-
3Md	4-(^{t}Bu)C_6H_4	quant (95)	-
3Me	3,4-$^{cy}(CH_2)_2C_6H_3$	quant (97)	-
3Mf	4-(O^{t}Bu)C_6H_4	-	65 (46)
3Mg	2-(F)C_6H_4	15 (8)	-
3Mh	4-(F)C_6H_4	80 (67)	-
3Mi	4-(Cl)C_6H_4	21 (17)	-
3Mj	4-(CF_3)C_6H_4	quant (93)	-
3Mk	3-(CO_2Me)C_6H_4	quant (98)	-
3Ml	4-(CO_2Me)C_6H_4	quant (93)	-
3Mm	4-(BPin)C_6H_4	88 (74)	-



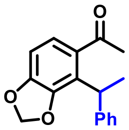
Prod.	R'	Yield 25 °C (%)	Yield 80 °C (%)
4Mn	H[f]	-	70 (54)
4Mo	Me[f]	2	13 (8)
4Mp	^{t}Bu	-	< 2
4Mq	$SiMe_3$	-	58 (55)
4Mr	$SiMe(OSiMe_3)_2$	-	39 (20)



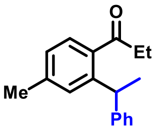
3Ua: 53 [4.8][d] (51) 7



3Va: 24 {9.8}[e] (21) 25



3Wa: quant (75) 15



3Xa: 82 (68) 58

[a] Reaction conditions: **1** (0.1 M, 1 equiv), **2** (0.1 M, 1 equiv), and **Co-Li** (10 mol %) in toluene at either 25 or 80 °C under N_2. ^1H NMR yields (%) are reported for 25 and 80 °C as the reaction temperatures and colored blue and red, respectively. [b] Isolated yields were determined from catalysis at 25 or 80 °C and are given in parentheses. [c] The ratio of regioisomers resulting from 2′- or 6′-C−H activation is given in square brackets. [d] The ratio of regioisomers resulting from 1′- or 3′-C−H activation is given in square brackets. [e] The ratio of branched (**3Va**) to linear (**4Va**) products is given in curly brackets. [f] An excess of ethylene or propylene (1 atm) was added.

Table 1. Imine Directing Group Scope[a]

substrate	Ar	^1H NMR yield (%)
1M	4-(OMe)C_6H_4 (PMP)	92
5	Ph	78
6	4-(CF_3)C_6H_4	63
7	2-(OMe)C_6H_4	17
8	2-(^{t}Bu)C_6H_4	0
9	3,5-(^{t}Bu$_2$)C_6H_3	72

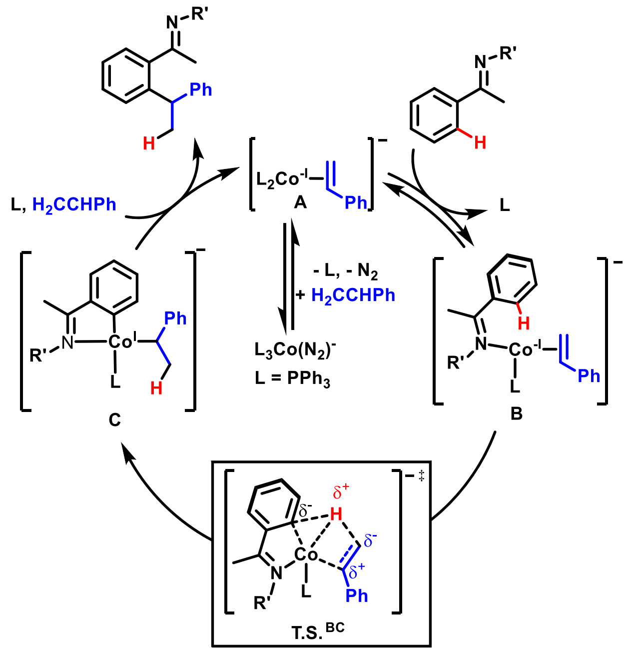
[a] Reaction conditions: (*N*-aryl)aryl imine **1M** or **5**−**9** (0.1 M, 1 equiv), **2a** (0.1 M, 1 equiv), and **Co-Li** (10 mol %) in toluene at 80 °C under N_2.

several advantages over systems that require *in situ* catalyst generation.[49] In the solid state, **Co-Li** remains catalytically active after storage for several months under an inert atmosphere at ambient temperatures; freshly prepared samples of **Co-Li** in benzene-d_6 remain identical over such periods (determined by ^1H NMR spectroscopy). In contrast, mixtures of CoX_2, phosphine, and Grignard reagents exhibit limited storability (hours) before catalyst degradation occurs. Perhaps the most important advantage to the single-component catalyst **Co-Li** is that reactive, nucleophilic activators are no longer required. Thus, for hydroarylation substrates bearing electrophilic functional groups (e.g., organic carbonyls), this catalyst provides excellent yields without generation of undesired side products. The precatalyst **Co-Li** was conveniently prepared on a gram scale by a synthetically straightforward three-step sequence, as described in earlier work from this laboratory.[49] Herein, the use of **Co-Li** as a versatile catalyst for olefin hydroarylations is described.

The two general catalytic conditions employed in this study were based on initial optimizations described for the alkyne hydroarylation system.[49] Catalytic reactions were examined under dilute substrate concentrations (0.1 M) in toluene with 10 mol % catalyst loading at either 25 or 80 °C.

On its own, efficient precoordination of acetophenone to the metal center does not occur; competent catalysis requires a better directing group, such as an N-coordinating imine. The imine substrates [**1A**−**1X** (Scheme 1)] were prepared by condensation of the corresponding substituted acetophenone with *p*-anisidine. The acid sensitivity of **Co-Li** necessitated preparation of the imine substrate prior to catalysis. Treatment of an equimolar mixture of acetophenone and *p*-anisidine with catalytic quantities of **Co-Li** resulted in rapid N−H deprotonation to generate the inactive complex, $(PPh_3)_3Co(N_2)H$, as has been discussed in a previous report.[49] The identity of the solvent does not affect the catalytic efficacy in

Scheme 3. Plausible Olefin Hydroarylation Mechanism[a]



[a]Li counterions have been omitted for the sake of clarity.

this system as determined with alkyne-based substrates.[49] The (*N*-aryl)aryl imine scope with styrene derivatives (**2a**−**2m**) or non-aromatic vinyl compounds (**2n**−**2r**) elucidated the generality of catalysis with **Co-Li**, as described in Scheme 2.

For the sake of clarity, branched products (**3**) and linear products (**4**) are encoded with two letters corresponding to the imine (first, uppercase) and olefin (second, lowercase) coupling partners. With **2a** as the olefin coupling partner, only branched products **3Aa**−**3Xa** were formed except in one case (*vide infra*). Generally, catalysis proceeded in higher yields at ambient temperatures.

Study of (*N*-aryl)aryl imine substrates possessing various *para* substituents (**1B**−**1O**) revealed several substitutional effects. Aliphatic or aromatic groups (**1B**−**1F**) distal to the N-coordinating imine did not affect the product yields (by ^{1}H NMR spectroscopy). The observed yields of products **3Ga**−**3Ia**, which were derived from substrates bearing halides, decreased as a function of C−X bond strength (i.e., F > Cl ≫ Br). Catalyst decomposition with substrates bearing weak C−X bonds may occur by LiX elimination. Indeed, there is precedent for rapid bond activations of this type with anionic metal fragments, as best illustrated by the reactivity of the Fp$^-$ anion with alkyl halides.[50] Such competing and nonproductive C−X activations irreversibly decompose the catalyst, thereby limiting the halide scope to F or Cl derivatives. Both electron-rich (**1B**−**1F**, **1K**, and **1L**) and electron-poor (**1G**, **1H**, **1J**, and **1M**) substrates were tolerated in good to excellent yields. In particular, substrate **1M** illustrated the advantage of this single-component catalyst; **1M** quantitatively converted to the hydroarylation product **3Ma** despite its reactivity with Grignard reagents. Substrates **1N** and **1O** proved to be problematic due to competitive binding through the N-coordinating substituent.

Catalysis with substrates bearing *meta* substituents (**1P**−**1W**) examined the regioselectivity of C−H cleavage (Scheme 1). With **1P**−**1T**, two distinct C−H bonds *ortho* to the imine directing group (i.e., 2′- or 6′-C−H) exist. The 3′-fluorine-containing substrate **1P** afforded a mixture of products resulting from 2′- and 6′-C−H bond cleavage in a ratio of 20:1. In contrast, hydroarylations with arene substrates bearing 3′-Me (**1R**), 3′-CF_3 (**1S**), or 3′-CO_2Me (**1T**) substitution afforded only one regioisomer functionalized at position 6′. The poorest regioselectivity occurred with naphthyl ethanimine **1U**, which possessed a slight preference for C−H activation at the 1′ site by a ratio of ∼5:1.

Heterocyclic aryl imines were tolerated, albeit in poor yields. Interestingly, benzofuran **1V** was the only substrate that afforded a mixture of branched and linear products (**3Va** and **4Va**, respectively) in a ratio of 9.8:1.0. Pyridyl- and thiophenyl-derived substrates were unreactive, likely due to the formation of stable N−E (E = S or N) chelates with the Co metal center. In contrast, **1W** bearing a 3′,4′-(methylenedioxy)phenyl skeleton underwent quantitative hydroarylation to form **3Wa**. A comprehensive list of inactive substrates tested in this study is given in Chart S1.

Substitutional effects in the styrene coupling partner were explored with substrates **2a**−**2m**; most of these olefins provided quantitative yields with the methyl ester containing imine **1M**. Nonquantitative yields occurred with only styrene derivatives bearing *ortho* (**2b** and **2g**) or halide (**2g**, **2h**, and **2i**) substituents. These examples are likely limited by either sterically congested metal centers or competitive C−X bond activations, respectively.

Other, non-styrene-derived olefins underwent catalytic hydroarylations, as evidenced by the formation of products **4Mn**−**4Mr**. Such olefins exclusively provided linear products, which is observed in other hydrofunctionalizations.[15,19,20,40,42,47] Good yields were observed with ethylene (**2n**) and vinyl silanes **2q** and **2r**. Unfortunately, the olefin scope possesses several limitations. Proximal steric bulk prohibits efficient catalysis by inhibiting olefin coordination, as evidenced with *tert*-butyl ethylene (**2p**). Internal olefins do not undergo catalysis (e.g., *cis*-*β*-methylstyrene or *cis*-2-butene). Long chain olefins (e.g., 1-octene) undergo rapid isomerization to form internal alkenes, thereby rendering the substrate inert.

Finally, the identity of the aryl moiety on the N-coordinating directing group affected the catalytic yields (Table 1). Electron-rich *N*-aryl groups led to higher yields than electron deficient directing groups (i.e., **1M** > **5** > **6**). The steric environment proximal to the N-coordinating imine appeared to dictate coordination to the metal center. *Ortho*-substituted aryl groups (**7** and **8**) provide a sterically inaccessible imine, thus precluding catalytic activity. These steric effects are somewhat mitigated if the steric bulk is distal to the N atom (**9**). Overall, *p*-methoxyphenyl (PMP) as the donor group provided the best yields.

A plausible mechanism for olefin hydroarylations catalyzed by **Co-Li** is given in Scheme 3. A mechanism similar to that described for alkyne hydroarylations is likely operative.[49] As a hydroarylation precatalyst **Co-Li** is converted to an active species via an initial coordination of the olefin (**A**), which displaces PPh_3 and N_2 ligands. Subsequent coordination of the imine affords **B**, which may undergo a CMD-like proton transfer (**T.S.**$^{\mathbf{BC}}$) to form a species akin to **C**. Reductive elimination from **C** produces the observed hydroarylation product and regenerates the active catalyst.

In conclusion, a versatile, single-component Co(-I) catalyst for olefin hydroarylations has been applied to more than 40 substrates in good to excellent yields, without undesired side

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product generation. This easily prepared and highly storable catalyst provides a new route for C−C bond formation with substrates bearing electrophilic functional groups that are incompatible with nucleophilic co-reagents. Generally high yields were observed under mild conditions for substrates bearing a variety of electronic and steric environments. Only branched products existed in the catalysis with styrene-derived olefins; in contrast, linear products were exclusively observed with vinyl silane substrates. Given the well-defined nature of the Co(-I) catalyst, it may be possible to directly tune the reactivity through modification of the phosphine ligand or the countercation. One such avenue of interest is the development of an enantioselective catalyst; this may be achieved through the use of *P*-chiral phosphine ligands or by the addition of chiral information to the participatory Li cation in the form of a chiral crowning reagent. Further developments are currently ongoing in this laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00258.

Experimental details and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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