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Cobalt(III)-Catalyzed Direct *ortho*-Alkenylation of Arylpyrazoles: A Comparative Study on Decarboxylation and Desilylation

Anil Kumar,[a] Nachimuthu Muniraj,[a] and Kandikere Ramaiah Prabhu*[a]

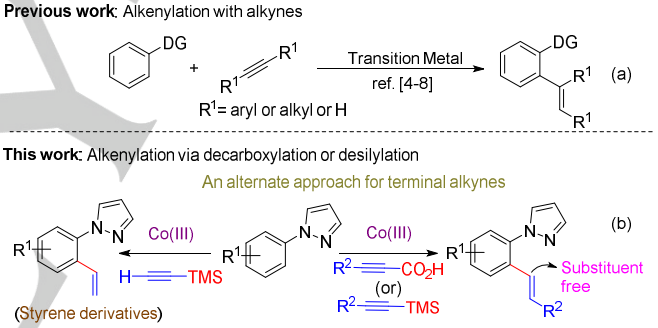
Dedication ((optional))

Abstract: A comparative study on Co(III)-catalyzed direct C-H bond alkenylation of 1-phenylpyrazole derivatives with alkynyl carboxylic acids and arylalkynyl silanes under redox-neutral conditions has been disclosed. These methods show excellent selectivity with good to excellent yields. Trimethylsilylacetylene has been utilized as a vinyl source to obtain the corresponding styrene derivatives. The major differences between these two reactions are the decarboxylation proceeds in the presence of a base additive whereas the desilylation takes place in the presence of an acid additive. The developed methodologies are compatible with a variety of functional groups.

Introduction

Transition metal-catalyzed C-H activation leading to the functionalization of organic molecules has emerged as a powerful synthetic tool for installing desired functional groups of interest.[1] There is significant progress employing a directing group assisted C-H activation using second- and third-row transition metal-catalysts.[2] However, the first-row transition metal-catalysts, such as cobalt(III) has received great attention in recent years.[3] C-H bond activation strategy is an efficient method for incorporating the olefins into the substituted aromatics. Alkynes are the preferred precursors for the alkenylation reaction as they offer external oxidant-free conditions. In most of the studies, internal alkynes (diphenylacetylene derivatives) are widely used as coupling partners to obtain the trisubstituted olefin derivatives (Scheme 1a).[4-7] As compared to internal alkynes, the utility of terminal alkynes (phenylacetylene derivatives) to obtain the corresponding disubstituted olefin derivatives are limited.[8] However, recently Chen and Yu have reported Co(III)-catalyzed *ortho*-alkenylation of arenes and 6-arylpurines with terminal alkynes.[8a]

Transition metal catalyzed traditional decarboxylative cross coupling reactions of alkynylcarboxylic acids are well explored area in organic synthesis.[9] Recently, alkynyl carboxylic acids are getting considerable attention in C-H activation reactions as they are bench stable, readily synthesized, and have unique reactivity.[10] Surprisingly, arylalkynyl silanes were rarely studied as a coupling partner in the transition-metal catalyzed C-H activation reactions.[11] Moreover, one of the easiest ways of obtaining aryl acetylene derivatives (terminal alkynes) are by either decarboxylation of the corresponding aryl alkynylcarboxylic acids or deprotection(desilylation) of aryl alkynyl silanes.[9c] Therefore, developing alkenylation reactions using alkynyl carboxylic acids or alkynyl silanes instead of terminal alkynes could be a step economical process. Inspired by our previous results on alkenylation reactions[10b,11c] and continued interest on Co(III)-catalyzed directed reactions,[12] herein, we report a comparative study on the decarboxylative and the desilylative *ortho*-alkenylation of 1-phenylpyrazole derivatives using Co(III)-catalyst (Scheme 1b).



Scheme 1.Comparision of previous works with this work.

Results and Discussion

The optimization studies were started by treating 1-phenylpyrazole **1a** with phenylpropiolic acid **2a** in the presence of $MnBr(CO)_5$ as a catalyst, using various additives, and solvents (see the Supporting Information, Table-S-1). After several trials, we found that the corresponding *ortho*-alkenylated product **3aa** could be obtained in 34% yield. Since $MnBr(CO)_5$ catalyst is not effective for this transformation, we turned our attention to cobalt(III)-catalyst for the same transformation. The reaction of **1a** with **2a** in the presence of $Cp^*Co(CO)I_2$ (5 mol%) as a catalyst, $AgSbF_6$ (20 mol%) as an activator and NaOAc (20 mol%) as an additive in DCE solvent (2 mL) at 100 °C for 3 h furnished the corresponding alkenylated product **3aa** in 78% yield (entry 1, Table 1). The solvent screening studies revealed that TFE is the bestsuited solvent as it afforded the product **3aa** in 88% yield (entries 2-5). Changing the activators to $AgBF_4$ and $AgNTf_2$ rendered the product **3aa** in 80 and 87% yields, respectively (entries 6 and 7), whereas AgOAc provided the product **3aa** in low yield (45%, entry 8). Among the additives, NaOAc was found to be an effective additive (entries 9-11). Lowering the catalyst loading, increasing or decreasing the

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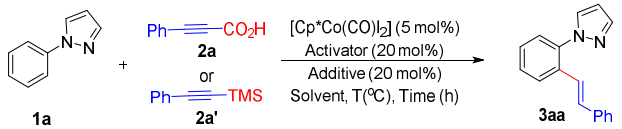
reaction temperature did not enhance the yield of **3aa** (entries 12-14). Reactions in the absence of Cp*Co(CO)I_2 catalyst or $AgSbF_6$ did not furnish the expected product **3aa** (entry 15 and 16), while the reaction in the absence of additive decreased the yield of **3aa** to 50% (entry 17). Reaction in the presence of Ru(II) was not useful, whereas reaction using Rh(III)-catalyst furnished the product **3aa** in 51% yield (entries 18 and 19).Next, we examined the reaction of **1a** with 1-phenyl-2-trimethylsilylacetylene **2a'** for the alkenylation reaction as **2a'** can be used as alternate for terminal alkynes. To our delight, the reaction of **1a** (0.2 mmol) with 1-phenyl-2-trimethylsilylacetylene **2a'** (0.24 mmol), Cp*Co(CO)I_2 (5 mol%) as a catalyst, $AgSbF_6$ (20 mol%) as an activator and Cl_3CCOOH (1.0 equiv) as an additive in TFE solvent (2 mL) at 100 °C for 3 h furnished the corresponding alkenylated product **3aa** in 83% isolated yield (entry 20, Table 1 and for detail optimization studies see the Supporting Information, Table-S-2).

Table 1. Optimization studies.[a]

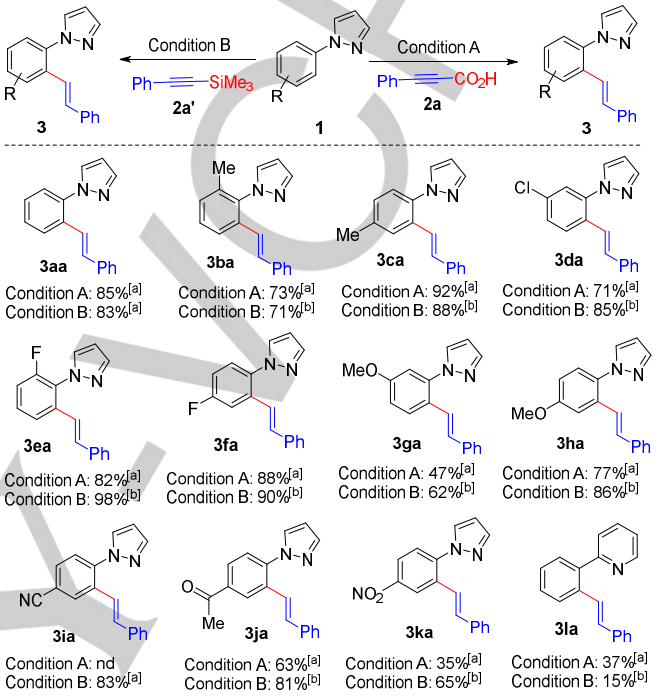


entry	activator	additive	solvent	time (h)	NMR yield **6aa** (%)[b]
1	$AgSbF_6$	NaOAc	DCE	3	78
2	$AgSbF_6$	NaOAc	THF	3	53
3	**$AgSbF_6$**	**NaOAc**	**TFE**	**3**	**88 (85)[c]**
4	$AgSbF_6$	NaOAc	toluene	3	78
5	$AgSbF_6$	NaOAc	dioxane	3	67
6	$AgBF_4$	NaOAc	TFE	3	80
7	$AgNTf_2$	NaOAc	TFE	3	87
8	AgOAc	NaOAc	TFE	3	45
9	$AgSbF_6$	KOAc	TFE	3	86
10	$AgSbF_6$	CH_3CO_2H	TFE	3	85
11	$AgSbF_6$	PivOH	TFE	3	80
12[d]	$AgSbF_6$	NaOAc	TFE	3	69
13[e]	$AgSbF_6$	NaOAc	TFE	12	73
14[f]	$AgSbF_6$	NaOAc	TFE	12	88
15[g]	$AgSbF_6$	NaOAc	TFE	3	nd
16	none	NaOAc	TFE	3	nd
17	$AgSbF_6$	none	TFE	3	50
18[h]	$AgSbF_6$	NaOAc	TFE	3	nd
19[i]	$AgSbF_6$	NaOAc	TFE	3	51
20[j]	**$AgSbF_6$**	**Cl_3CCOOH**	**TFE**	**3**	**86 (83)[c]**

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), [Cp*Co(CO)I_2] (5 mol%), activator (20 mol%), additive (20 mol%), solvent (2 mL), at 100 °C for 3 h. [b]^{1}H NMR yield using terephthaldehyde as an internal standard. [c] Isolated yield. [d] 2.5 mol% [Co(III)] catalyst was used. [e] Reaction at 80 °C. [f] Reaction at 120 °C. [g] in absence of Co(III) catalyst. [h] [Ru(p-cymene)Cl_2]$_2$ was used. [i] [RhCp*Cl_2]$_2$ was used. [j] reaction with **2a'**. nd = not detected. PivOH = pivalic acid.

Having two different methods in hand (entries 3 and 20, Table 1) for *ortho*-alkenylation of 1-phenylpyrazole **1a**, we started a comparative study on decarboxylative and desilylative alkenylation of 1-phenylpyrazolederivatives **1** (Table 2). Thus, precursors having alkyl, halogen, and methoxy substitution on the various positions of the phenyl ring of **1**, reacted smoothly with phenylpropiolic acid **2a** as well 1-phenyl-2-trimethylsilylacetylene **2a'** furnishing the corresponding alkenylated products **3aa-3ha** in good to excellent yields. The reaction of 4-(1H-tyrazol-1-yl)benzonitrile**1i** with phenylpropiolic acid was not successful while the same reaction of **1i** with 1-phenyl-2-trimethylsilylacetylene furnished the product **3ia** in 83% yield. Electron withdrawing groups such as acetyl and nitro groups on 1-phenylpyrazole were compatible under both the reaction conditions furnishing the products **3ja** and **3ka** in moderate to good yields. The reaction of 2-phenylpyridine with the phenylpropiolic acid and 1-phenyl-2-trimethylsilylacetylene furnished the product **3la** in 37 and 15% yields, respectively.

Table 2.Scope for 1-phenylpyrazole derivatives.



Condition A: **1a** (0.2 mmol), **2a** (0.24 mmol), [Cp*Co(CO)I_2] (5 mol%), $AgSbF_6$ (20 mol%), NaOAc (20 mol %), TFE (2 mL), at 100 °C for 3 h. **Condition B**: **1a** (0.2 mmol), **2a'** (0.24 mmol), [Cp*Co(CO)I_2] (5 mol%), $AgSbF_6$ (20 mol%), Cl_3CCO_2H (1.0 equiv), TFE (2 mL), at 100 °C for 3 h. [a] Isolated yield. [b]^{1}H NMR yield using terephthaldehyde as an internal standard.

The scope of the reaction has been extended by reacting **1a** with various arylalkynyl carboxylic acid derivatives**2** (Table 3). Thus, alkyl, methoxy and halo-substituted arylalkynyl carboxylic acids reacted smoothly with **1a** furnishing the corresponding *ortho*-alkenylated products **4aa-4ag**in good yields. Synthetically useful functional groups such as cyano, nitro, acetyl and ester groups at the *para*-position of arylalkynyl carboxylic acid are well-tolerated affording the products **4ah-4ak** in good to excellent yields. Thiophene derived alkynyl carboxylic acid underwent a smooth reaction with **1a** yielding the product **4al** in 62% yield. Alkylalkynyl carboxylic acids such as 2-butynoic acid reacted with **1a** furnishing the mono-alkenylated product **4am** in 65% yield. The reaction of **1a** with 2-hexynoic acid furnished a mixture of mono- and di-alkenylated products **4an** and **4an'** in 29 and 14% yields, respectively.

The scope of the reaction was further explored by the reaction of **1a** with a few arylalkynyl silane derivatives**2'** (Table 4). The reaction of **1a** with arylalkynyl silane derivatives having alkyl, methoxy, and halo substitution at the *para*-position furnished the corresponding *ortho*-alkenylatedproducts **4aa-4ac** in good to excellent yields. A methyl substituent at the *ortho*-position or a bulky group *tert*-butyl group at the *para*-position afforded the corresponding alkenylated products **4af** and **4ag** in 80 and 73% yields, respectively. Different functional groups like

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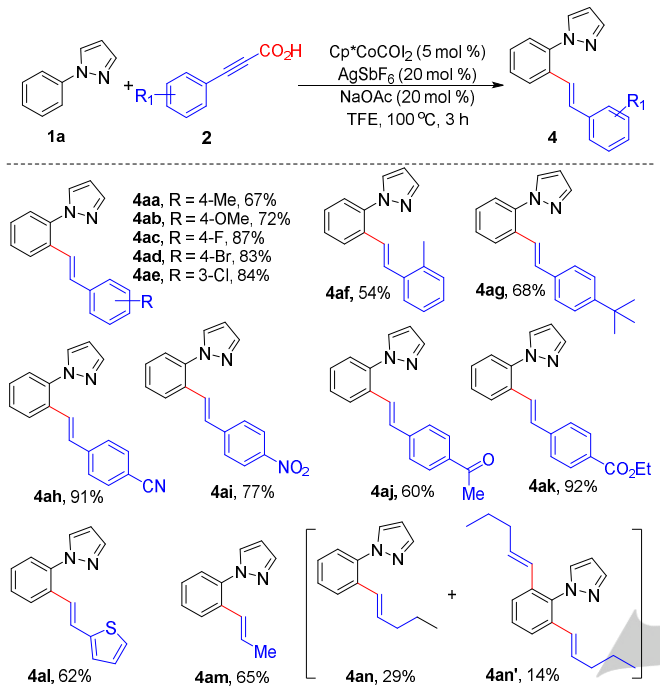
cyano, nitro, and ester groups at *para*-position on the phenyl ring are also well tolerated forming the products **4ah**, **4ai**, and **4ak** in 89, 81, and 85% yields, respectively. The thiophene derived alkynyl silane furnished the corresponding alkenylated product **4al** in moderate yield of 53%.

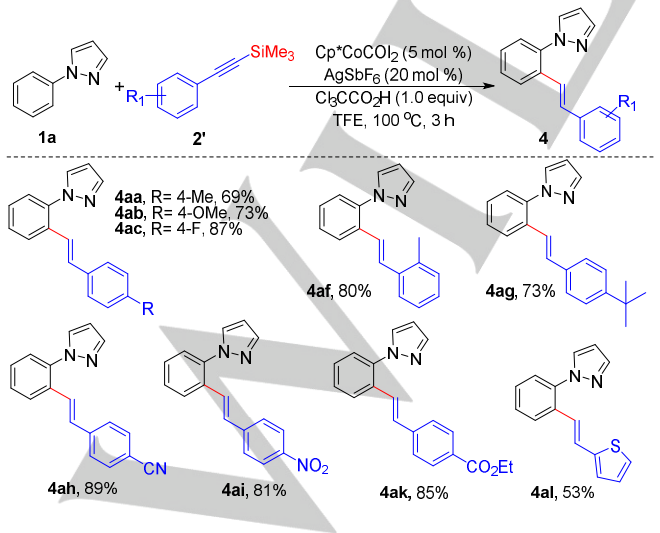
Table 3. Scope for alkynyl carboxylic acid derivatives.[a,b]



[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), [Cp*Co(CO)I$_2$] (5 mol%), [AgSbF$_6$] (20 mol%), NaOAc (20 mol%), TFE (2 mL), at 100 °C for 3 h. [b] Isolated yields.

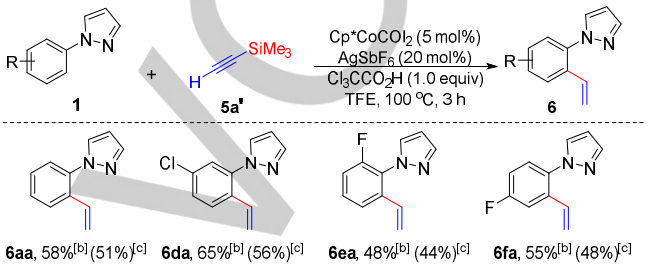
From this experimental study, we found that the reactivity of both arylalkynyl carboxylic acid derivatives and arylalkynyl silane derivatives are similar and complimentary to each other. Next, we attempted to extend the scope of the reaction using propiolic acid **5a** and trimethylsilyl acetylene **5a'**to obtain the corresponding styrene derivatives. The reaction of propiolic acid **5a** with **1a** under the optimal reaction conditions furnished the product **6aa** in low yield of 25% (see Supporting Information, Table-S-3), whereas the reaction of trimethylsilylacetylene **5a'**with **1a** under the optimal conditions furnished the product **6aa** in moderate yield of 58%(see Supporting Information, Table-S-4).

Table 4. Scope for alkynyl silane derivatives.[a,b]



[a]Reaction conditions: **1a** (0.2 mmol), **2'** (0.24 mmol), [Cp*Co(CO)I$_2$] (5 mol%), [AgSbF$_6$] (20 mol%), Cl_3CCO_2H (1.0 equiv), TFE (2 mL), at 100 °C for 3 h. [b] Isolated yields.

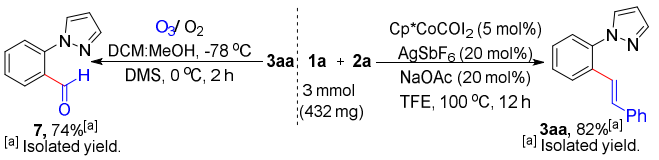
Table 5. Substrate scope for 1-phenylpyrazole derivatives.[a]



[a]Reaction conditions: **1a** (0.3 mmol), **5a'** (0.36 mmol), [Cp*Co(CO)I$_2$] (5 mol%), [AgSbF$_6$] (20 mol%), Cl_3CCO_2H (1.0 equiv), TFE (3 mL), at 100 °C for 3 h. [b] Isolated yield. [c] NMR yield using terephthaldehyde as an internal standard.

Further optimization of reaction conditions was not helpful in improving the yield of **6aa** (see Supporting Information, Table-S-4). This protocol was useful for halogen substituted 1-phenylpyrazole derivatives, which gave moderate to good yields **6aa-6fa** (Table 5).However, 1-phenylpyrazoles having substituents such as methoxy, nitro, cyano, and keto groups on phenyl ring also furnished a good yield of the *ortho*-alkenylated products **6ga-6ka** as inseparable mixture with their corresponding 1-phenylpyrazole derivatives (See Supporting Information, Scheme-S-1). A few unsuccessful substrates for the *ortho*-alkenylation reactions are also listed in the supporting information (see SI, Scheme-S-2).

Scheme 2. Synthetic utility and scaling-up reaction.



Further, to demonstrate the usefulness of the alkenylated products, *ortho*-alkenylated product **3aa** was subjected to ozonolysis to obtain the corresponding aldehyde **7** in 74% yield (Scheme 2). A scaling-up experiment of **1a** (3 mmol, 432 mg) with phenylpropiolic acid **2a** under the optimum reaction conditions afforded the corresponding product **3aa** in 82% isolated yield (Scheme 2).

To probe the reaction mechanism, a few control experiments were performed (Scheme 3). 1-(p-Tolyl)-1H-pyrazole **1c** on treatment with D_2O under optimal reaction conditions did not lead to the deuteration of *ortho*-hydrogens of

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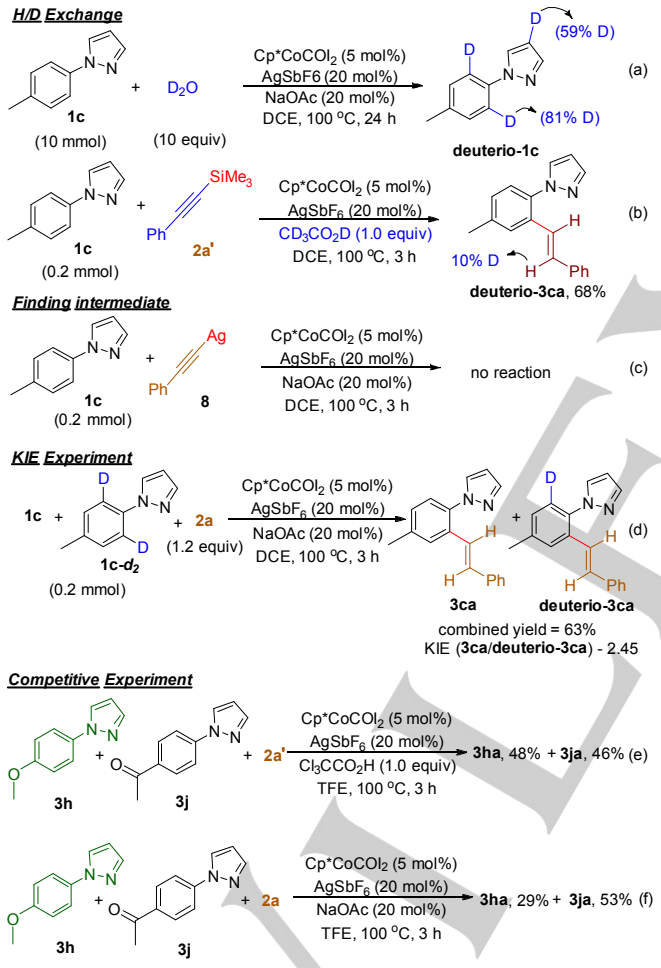
1c, whereas the same deuteration experiment, using DCE as a solvent, showed 81% deuteration at the *ortho*-positions of **1c** (see SI and Scheme 3a). Since, DCE was also found to be an effective solvent for this transformation, further control experiments were carried out in DCE solvent. The reaction of **1c** with 1-phenyl-2-trimethylsilylacetylene **2a'** using CD_3CO_2D as an acid additive led to the deuteriumin corporation on the olefinic carbon of the product **3ca** (10% D, Scheme 3b) indicating the involvement of the acid additive in the protodemetallation step. To find out whether silver phenylacetylide **8** is an intermediate, we performed a reaction of **1c** with silver phenylacetylide **8**, which failed to give the product **3ca** (Scheme 3c). This experiment rules out the intermediacy of silver phenylacetylide. The Kinetic Isotopic Effect (KIE) value of 2.45 observed in the reaction of **1c** and **1c-*d*$_2$** with **2a** suggested that the C-H activation step could be a rate-determining step (Scheme 3d). A

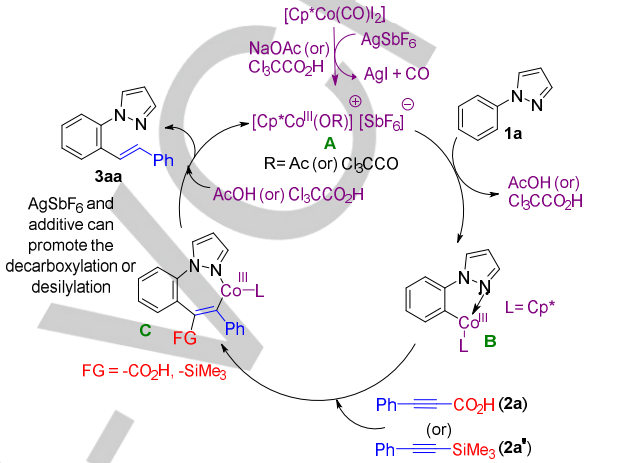
Scheme 3. Control experiments for mechanistic studies.



competitive reaction of electronically different pyrazole derivatives **3h** and **3j** with alkynyl silane **2a'** exhibited an almost equal reactivity (Scheme 3e). However, the similar reaction of pyrazole derivatives **3h** and **3j** with alkynylcarboxylic acid **2a** favors the electron poor **3j** (Scheme 3f).

Based on the control experiments, our previous studies,[10b,11c] and the literature precedence,[5-8] a plausible mechanism has been proposed (Scheme 4). An *in situ* generated catalytically active species **A** reacts with **1a** leading to the cobaltacycle **B**. Insertion of alkyne **2a** or **2a'** to the **B** forms the 7-membered intermediate **C**. From intermediate **C** the decarboxylation[10b] or desilylation[11c] takes place in the presence of $AgSbF_6$/additive followed by subsequent protodemetallation with the help of acid allows the desired product **3aa** along with the active catalyst **A**.

Scheme 4. Plausible Mechanism



Conclusions

In conclusion, a Co(III)-catalyzed *ortho*-alkenylation of 1-phenylpyrazole derivatives using arylalkynyl carboxylic acid derivatives and arylalkynyl silane derivatives as a coupling partner through decarboxylation and desilylation routes have been studied. In this study, we found that the alkynylcarboxylic acids and arylalkynylsilanes, which have electronically different environment, furnished the same products in excellent selectivity with high yields. Both the coupling partners can serve as alternate to terminal alkynes in C-H activation reactions, which are complementary to each other. Additionally, trimethylsilyl acetylenes have also been utilized as a vinyl source to obtain the corresponding styrene derivatives.

Experimental Section

(a) Procedure for *ortho*-alkenylation of arylpyrazole derivatives with arylalkynyl carboxylic acids derivatives

In a 8-mL screw-cap reaction vial, arylpyrazole derivative (0.2 mmol), arylalkynyl carboxylic acid (0.24 mmol), cobalt catalyst [Cp^*CoCOI_2], (4.8 mg, 5 mol%), NaOAc (3.3 mg, 20 mol%), $AgSbF_6$ (13.4 mg, 20 mol%) in TFE solvent (2 mL) were taken. The vial was sealed with a screw cap and placed on a pre-heated metal block at 100 °C and the reaction mixture was stirred at the same temperature for 3 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, filtered through a silica pad using a mixture of EtOAc and petroleum ether (1:1, 100 mL), and concentrated under vacuum. The crude products were submitted directly for ^{1}H NMR analysis for calculating the ^{1}H NMR yields, terephthalaldehyde (0.1 mmol, 13.4 mg) has been used as an internal standard. The crude products were purified on a silica gel column using EtOAc/petroleum ether mixture.

(b) Procedure for *ortho*-alkenylation of arylpyrazole derivatives with 1-phenyl-2-trimethylsilylacetylene derivatives

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In a 8-mL screw cap reaction vial, arylpyrazole derivative (0.2 mmol), 1-Phenyl-2-trimethylsilylacetylene derivative (0.24 mmol), cobalt catalyst $[Cp^*CoCOI_2]_2$(4.8 mg, 5 mol%), Cl_3CCO_2H (33.0 mg, 100 mol%), $AgSbF_6$ (13.4 mg, 20 mol%) in TFE solvent (2 mL) were taken. The vial was sealed with a screw cap and placed on a pre-heated metal block at 100 °C and the reaction mixture was stirred at the same temperature for 3 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, filtered through a silica pad using a mixture of EtOAc and petroleum ether (1:1, 100 mL), and concentrated under vacuum. The crude products were submitted directly for ^{1}H NMR analysis for calculating the NMR yields, terephthalaldehyde (0.1 mmol, 13.4 mg) has been used as an internal standard. The crude products were purified on a silica gel column using EtOAc/petroleum ether mixture.

(c) Procedure for *ortho*-alkenylation of arylpyrazole derivatives with trimethylsilylacetylene

In a 8-mL screw cap reaction vial, aryl pyrazole derivative (0.3 mmol), trimethylsilylacetylene (0.36 mmol), cobalt catalyst $[Cp^*CoCOI_2]_2$(7.2 mg, 5 mol%), Cl_3CCO_2H (49.5 mg, 100 mol%), $AgSbF_6$ (20.1 mg, 20 mol%) in TFE solvent (3 mL) were taken. The vial was sealed with a screw cap and placed on a pre-heated metal block at 100 °C and the reaction mixture was stirred at the same temperature for 3 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, filtered through a silica pad using a mixture of EtOAc and petroleum ether (1:1, 100 mL), and concentrated under vacuum. The crude products were submitted directly for ^{1}H NMR analysis for calculating the NMR yields, terephthalaldehyde (0.15 mmol, 13.4 mg) has been used as an internal standard. The crude products were purified on a silica gel column using DCM/petroleum ether mixture.

(d) Procedure for synthesizing compound 7

In a 25 mL round bottom flask, ozone was bubbled through a pre-cooled (-78 °C) solution of **3aa** (49.5 mg, 0.20 mmol) and a pinch of $NaHCO_3$ in DCM:MeOH (9:1, 10 mL), until the pale blue colour persisted. Excess of ozone was flushed off with oxygen and was added dimethyl sulphide (0.5 mL). The reaction mixture was warmed to 0 °C and stirred at the same temperature for 2 h. The reaction mixture was concentrated under reduced pressure and the crude mixture was purified on a silica gel column using EtOAc/petroleum ether mixture to afforded the product **7** in 74% yield.

Acknowledgements

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Keywords: arylpyrazole**;** arylalkynyl carboxylic acids; 1-phenyl-2-trimethylsilylacetylene; C-H Activation.

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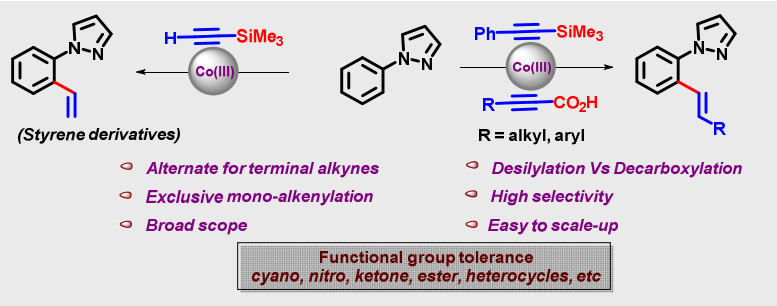

Decarboxylation and Desilylation*

*Anil Kumar, Nachimuthu Muniraj, and Kandikere Ramaiah Prabhu**

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Cobalt(III)-Catalyzed Direct *ortho*-Alkenylation of Arylpyrazoles: A Comparative Study on Decarboxylation and Desilylation

A comparative study on Co(III)-catalyzed direct C-H bond alkenylation of 1-phenylpyrazole derivatives with alkynyl carboxylic acids and arylalkynyl silanes under redox-neutral conditions has been studied. Trimethylsilylacetylene has been utilized as a vinyl source to obtain the corresponding styrene derivatives. The developed methodologies are compatible with a variety of functional groups.

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