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1. Introduction

In the past decade, transition metal catalysis has been recognized as a powerful synthetic tool for diarylmethanols through the addition of organometallic reagents.^{1,2} Organogermanes³ have received much less attention so far, compared with their congeners such as organosilanes⁴ and organostannanes due to their lower reactivity, the higher cost of germanium relative to silicon⁵ and the less reported synthetic methodology of organogermanes.5-9 To the best of our knowledge, organogermanes are more susceptible to breaking the C-Ge bond than arylsilane analogues,9 and have lower carbon-metal bond energy and a larger covalent radius than their silicon counterparts in group IVA. However, examples of employing aryltrimethylgermanes in addition reactions have been never reported before. Our previous work¹⁰ prompted us to explore the possibility of employing low-cost catalysts in addition reactions. Herein, we report our preliminary results on the first example of cobalt-catalyzed addition of aromatic aldehydes and arylglyoxals with ArGeMe₃ using a CoI₂/tmphen catalytic system.

The reaction of $PhGeMe_3$ (1a) and 4-nitrobenzaldehyde (2a) was firstly chosen as the model reaction for this cobalt-catalyst system (Fig. 1).

Ligands were firstly screened since it often plays an important role in transition-metal-catalyzed chemistry.⁹ The effects of phosphine ligand with different electron-donating, electronwithdrawing and steric hindrance groups were examined (Fig. 1, L1–L4), but no target product was detected. However, the yield of **3a** could be improved to 80% when the combination of CoCl₂ and **tmphen** (L8) was employed (Fig. 1, L8). Subsequently, various reaction conditions concerning the types and amount of cobalt sources, the effects of time and temperature, bases, solvents, were examined to increase the yield of product

Co-catalyzed arylation of aldehydes and aryltrimethylgermanes†

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A novel cobalt-catalyzed protocol for the synthesis of carbinol derivatives and benzil derivatives has been developed. In the presence of Col₂ as the catalyst and **tmphen** (3,4,7,8-tetramethyl-1,10-phenanthroline) as the ligand, the corresponding arylated products were obtained from the addition of aryltrimethylgermanes to aromatic aldehydes and arylglyoxals in moderate to excellent yields under air atmosphere.

(Table 1). After extensive screening, the optimized reaction condition was established as follows: CoI_2 (2.5 mol%), **tmphen** (L8, 2.5 mol%), K_2CO_3 (1.0 mmol), THF (3.0 mL), ArGeMe₃ (0.65 mmol) and aldehydes (0.5 mmol), 65 °C, 12 h. Among the bases we used, K_2CO_3 was superior to other bases such as NaHCO₃, Na₂CO₃, NaOAc, KF, Li₂CO₃, and Cs₂CO₃. 14% yield of benzophenone was detected when using Cs₂CO₃ as the base under model reaction condition (Table 1, entry 7). The choice of solvents was also crucial to the reaction. THF was proved to be the best one of all the solvents we chosed.

Subsequently, various reaction conditions concerning the types and amounts of cobalt sources, the effects of time and temperature, bases, solvents, were examined to increase the yield (Table 1). After extensive screening, the optimized reaction condition was established as follows: CoI_2 (2.5 mol%), **tmphen** (L8, 2.5 mol%), K₂CO₃ (1.0 mmol), THF (3.0 mL), ArGeMe₃ (0.65 mmol) and aldehydes (0.5 mmol), 65 °C, 12 h. Among the bases we used, K₂CO₃ was superior to other bases such as NaHCO₃, Na₂CO₃, NaOAc, KF, Li₂CO₃, and Cs₂CO₃. 14% yield of benzophenone was detected when using Cs₂CO₃ as the base under



^[a] All reactions were conducted with PhGeMe₃ (126 mg, 0.65 mmol), 4nitrobenzaldehyde (53 mg, 0.5 mmol), K₂CO₃ (138 mg, 1.0 mmol), CoCl₂ (3.3 mg, 5 mol %), and ligand (5 mol %) in 3 mL of THF at 65 °C for 24 h, under air atmosphere. ^[b] Yields of isolated products after chromatography.

Fig. 1 Ligand screening.^a

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Table 1 Selected results for the optimal reaction conditions^a



Entw	Catalwat	Paga	Colvent	Viold ^b (0()
Entry	Catalyst	Base	Solvent	field (%)
1	_	_	THF	N.R
2	$CoCl_2$	_	THF	N.R
3	$CoCl_2$	NaHCO ₃	THF	21
4	$CoCl_2$	Na_2CO_3	THF	51
5	$CoCl_2$	NaOAc	THF	28
6	$CoCl_2$	KF	THF	53
7	$CoCl_2$	Cs_2CO_3	THF	71
8	$CoCl_2$	K_2CO_3	THF	80
9	$CoCl_2$	K_2CO_3	DME	62
10	$CoCl_2$	K_2CO_3	CH ₃ CN	<5
11	$CoCl_2$	K_2CO_3	DMF	<5
12	$CoCl_2$	K_2CO_3	Dioxane	37
13 ^c	CoI ₂	K_2CO_3	THF	92
14^d	CoI_2	K_2CO_3	THF	90
15	CoI ₂	K_2CO_3	THF	87
16	CoBr ₂	K_2CO_3	THF	67
17	$Co(OAc)_2$	K_2CO_3	THF	58
18	$Co(C_5H_5)_2$	K_2CO_3	THF	14
19	Co_3O_4	K_2CO_3	THF	<5
20	$PdCl_2$	K_2CO_3	THF	<5
21	$RhCl_3 \cdot 3H_2O$	K_2CO_3	THF	<5

^a Reaction conditions: 1 (126 mg, 0.65 mmol), 2 (76 mg, 0.5 mmol), cobalt source (5 mol%), tmphen (L8, 5.9 mg, 5 mol%); base (1.0 mmol), solvent (3 mL), 65 °C for 12 h, under air in reaction tubes. ^b Yields of isolated products after chromatography. ^c CoI₂ (3.9 mg, 2.5 mol%), **tmphen** (L8, 3.0 mg, 2.5 mol%). ^d CoI₂ (15.6 mg, 10 mol%), tmphen (L8, 11.8 mg, 10 mol%).

model reaction condition (Table 1, entry 7). The choice of solvents was also crucial to the reaction. THF was proved to be the best one of all the solvents we chosed.

With the optimized conditions in hand, a variety of aldehydes with electron-rich, electron-deficient and steric hindrance was examined to broaden the extent of the reaction. Typical functional groups such as methyl, methoxyl, fiuoro, chloro were well tolerated under the reaction conditions. Electron-deficient analogues of aldehyde reacted with ArGeMe₃ easily and gave biarylmethanols in good yields (Table 2, entries 1-10). Particularly, 4-formylbenzaldehyde could react with PhGeMe₃ and the product of **3n** and keep one formyl group untouched (Table 2, entry 14). The chloro and bromo groups untouched in this catalytic system (Table 2, entries 9 and 10). Unfortunately, the reaction was stopped by using aldehydes with neutral and electron-rich groups or aliphatic aldehydes due to its low activity to aryltrimethylgermane under this reaction condition. However, butyraldehyde or 4-methoxybenzaldehyde as substrate react with phenyltrimethylgermane did not give the responding products. Similarly, tetramethylgermane as substrate react with 4-nitro-phenyladehyde also did not give the responding products.

 Table 2
 Selected results for the optimal reaction conditions^a

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8



Paper

Table 2 (Contd.)



^{*a*} Reaction conditions: ArGeMe₃ **1** (0.65 mmol), aldehyde **2** (0.5 mmol), CoI₂ (3.9 mg, 2.5 mol%), **tmphen** (**L8**, 3.0 mg, 2.5 mol%), K₂CO₃ (138 mg, 1.0 mmol), THF (3 mL), 65 °C for 12 h, under air in pressure tubes. ^{*b*} Yields of isolated products after chromatography.

During broadening the extent of the reaction, the phenylglyoxal hydrate was examined to broaden the scope of the reaction, which could be seen as the electron-deficient analogue instead of 4-nitrobenzaldehyde. Only a trace of benzoin formed, the benzil was instead the major final product. Obviously, benzil was resulted from catalytic oxidation of in situ generated benzoin in the presence of K₂CO₃ in air. It was noteworthy that the over oxidation product could not be detected under argon atmosphere with degassed THF. A more efficient catalytic system with the dual ability to facilitate the addition of ArGeMe₃ to phenylglyoxal hydrate was obtained when K₂CO₃ was exchange by Cs_2CO_3 as the base. Then, the optimized reaction conditions were then extended to conversions of PhGeMe₃ to phenylglyoxal hydrate as follows: CoI2 (3.9 mg, 2.5 mol%), tmphen (L8, 3.0 mg, 2.5 mol%), Cs₂CO₃ (326 mg, 1.0 mmol), THF (3.0 mL), PhGeMe₃(0.65 mmol) and phenylglyoxal hydrate (0.5 mmol), 65 °C, 12 h (Table 3).

The reactions of different ArGeMe₃ with arylglyoxals were examined to broaden the scope of the reaction. All the reactions catalyzed by CoI₂/tmphen proceeded well and provided the desired products in good yields. Although the hetero-atoms in heteroaryltrimethylgermanes might coordinate the to transition-metal, trimethyl(thiophen-3-yl)germane and trimethyl(thiophen-2-yl)germane were still good partners for the addition reaction. The corresponding products were isolated in 67% and 59% yields, respectively (Table 3, entries 11 and 12). It seemed that the ortho substituents had little influence on their activities. For instance, (2-chlorophenyl)trimetrimethyl(o-tolyl)germane thylgermane. and trimethyl(naphthalen-1-yl)germane could react with phenylglyoxal hydrate to furnish 4j, 4k, and 4l in excellent yields (Table 3, entries 13-15). The comparison of PhGeMe₃ and its congener PhSiMe₃ was also investigated under the optimised reaction conditions. However, PhSiMe3 was not the proper candidates and recovered the reactants. Similarly, tetramethylgermane as substrate to react phenylglyoxal hydrate did not give the responding products.

To further understand the mechanism, the model reaction under optimized reaction conditions was studied by gas chromatography-mass spectrometry. The data showed that 1,1'biphenyl and hexamethyldigermane were the by-products, except for the addition product and the reactants. To account for the present reaction, a plausible mechanism based upon the above experimental results was proposed as follows (Fig. 2).

A plausible mechanism for forming diarylmethanols (Fig. 2): the catalytic cycle may contain three steps: Co(II) undergoes transmetallation to form ArCo(II)IL (**A**), which exhibits high nucleophilicity toward carbonyl carbon might produce the byproduct with 1,1'-diphenyl and hexamethyldigermane through cross-coupling reaction. Then arylcobalt¹¹ should be transferred to carbonyl carbon through the insertion gives the intermediate (**B**). Finally, the hydrolysis of intermediate (**B**) affords the diarylmethanols. Cs_2CO_3 might facilitate the addition of aryltrimethylgermane to arylglyoxal and prompt the aerobic oxidation of the carbinol; The ICo–OH species reacts with I⁻ to regenerate the active CoI_2 for the next cycle.

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Table 3 (Contd.)





In summary, we describe here the first time a mild cobaltcatalyzed nucleophilic arylation of aromatic aldehydes and arylglyoxals with ArGeMe₃ using CoI₂/tmphen catalytic system. In the presence of CoI₂/tmphen catalytic system, a variety of electron-deficient arylaldehydes and arylglyoxals was found to be suitable substrates for the reaction with ArGeMe₃ in moderate to excellent yields. It was noteworthy that our methodology could keep the formyl group chloro and bromo groups untouched for further functionalization. This method might provide potential opportunities for the addition of ArGeMe₃ to unsaturated carbon–carbon bonds and unsaturated carbonhetero bonds. The detailed mechanism of the reaction and further applications of ArGeMe₃ are the focus of ongoing efforts in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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