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Rh-Catalyzed Carbonylation of Arylzinc Compounds Yielding Symmetrical Diaryl Ketones by the Assistance of Oxidizing Agents

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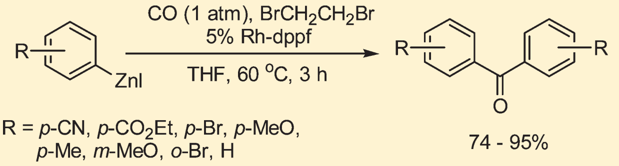
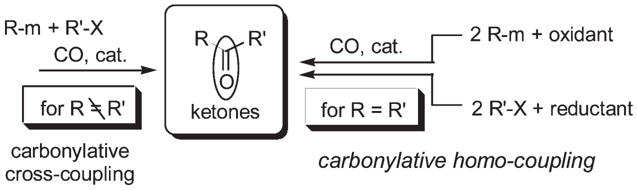
S Supporting Information

ABSTRACT: Carbonylative homocoupling of arylzinc compounds **1** using 1 atm of CO and 1,2-dibromoethane as an oxidant was achieved in the presence of Rh−dppf catalyst, affording symmetrical diaryl ketones in good yields. Under similar conditions, Pd or Ni catalysts induced oxidative homocoupling of **1** to yield biaryls instead. The beneficial catalysis by Rh in the carbonylation was presumed to stem from the facility by which the migration of the aryl ligand to CO at the Rh^{3+} intermediate occurred.



Carbon monoxide serves as a versatile and straightforward building block to construct the CO segment in ketones through catalytic cross-coupling between organometallic nucleophiles R-m and carbon electrophiles R'-X, accompanied by the insertion of carbon monoxide (Scheme 1).[1] This carbonylative cross-coupling is valuable in organic syntheses since it not only retains the beneficial properties of cross-coupling, e.g., high efficiency and high chemoselectivity of the catalytic process, but also eliminates the need for carboxylic acid derivatives R'CO-X as carbon electrophiles, thus readily providing efficient access to polyfunctionalized ketones.[1,2] For the synthesis of symmetrical ketones, carbonylative homocouplings, available with single coupling components, e.g., R-m in oxidative reactions or R'-X in reductive reactions, should provide convenient alternatives for the carbonylative cross-coupling (Scheme 1). To our knowledge, the protocols used previously to achieve efficient catalytic reactions with various combinations of R-m with oxidizing agents[1a,3] or R'-X with reducing agents[1a,4] have been severely limited. In the course of our study on the synthesis and applications of arylzinc compounds ArZnX **1**,[5] we attempted the unprecedented catalytic carbonylation of **1** with the assistance of an oxidizing agent, with the intention of developing efficient and novel access to symmetrical diaryl ketones. Diaryl ketones are a prevailing structural motif in various fields including medicinal and pharmaceutical chemistry,[6] functional molecules,[7] and advanced materials[8] and are useful in molecular transformations as synthetic intermediates.[9]

Scheme 1. Synthesis of Ketones Utilizing Catalytic Carbonylative Couplings



The reaction of phenylzinc iodide **1a** with CO (1 atm) was examined in THF at 60 oC for 3 h in the presence of 10 mol % of catalyst and oxidizing agent (2 equiv). As shown in Table 1, utilizing 1,2-dibromoethane **2** as the oxidant, the reaction of **1a** took place smoothly under CO atmosphere by catalysis with Pd, Ni, or Rh to consume **1a** nearly quantitatively (entries 1−6). However, in runs using Pd or Ni catalysts, the reaction mainly took place between **1a** and **2**, and the oxidative homocoupling product, biphenyl **4a**, was obtained in high yield (entries 1−4). Fortunately, the Rh catalyst successfully achieved the concomitant insertion of CO, affording benzophenone **3a** in high yield (entry 5). Co catalyst also afforded **3a**, together with **4a** (entry 8).[10] For the Rh catalyst, 1,1′-bis(diphenylphosphino)ferrocene dppf was the best ligand among those examined (entries 5−7). As oxidants, O_2, $CuCl_2$, $Cu(OAc)_2$, and $ClCH_2CH_2Cl$ were less effective than **2** (entries 9−12). Even when the amounts of Rh-dppf catalyst and oxidant **2** were decreased to 2 mol % and 1.2 equiv, respectively, the yield of reaction product **3a** remained high (entries 13 and 14). Other arylmetallic compounds Ar-m (m = B, Sn, or Mg) were less effective than **1a** under the examined conditions (entries 15−17). As shown in Table 2, ArZnX **1** containing such functional groups as cyano (entry 2), alkoxycarbonyl (entry 3), bromo (entries 4 and 5), alkoxy (entry 6), or alkyl (entries 7 and 8) at ortho (entry 5), meta (entry 8), or para (entries 2−4, 6, and 7) positions took part in the desired reaction equally well. This Rh-catalyzed reaction is also applicable to a 2-thienylzinc compound (entry 9). Thus, by means of **1** and **2**, this is the first instance in which a Rh−dppf catalyst achieved carbonylative homocoupling of arylmetallic nucleophiles Ar-m by the assistance of oxidizing agents.[3a,3b] In contrast

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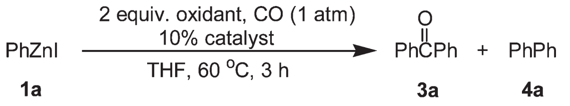
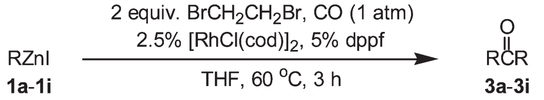
Table 1. Catalytic, Oxidative Homocoupling of 1a under CO Atmosphere[a]



entry	catalyst	oxidant	yield (%)[b] 3a	yield (%)[b] 4a
1	$PdCl_2(PPh_3)_2$	$BrCH_2CH_2Br$	15	80
2	PdCl2(dppf)	$BrCH_2CH_2Br$	33	
3	$NiCl_2(PPh_3)_2$	$BrCH_2CH_2Br$	<5	9
4	$NiCl_2(dppf)$	$BrCH_2CH_2Br$	6	76
5	$RhCl(PPh_3)_3$	$BrCH_2CH_2Br$	71	9
6	$1/2[RhCl(cod)]_2/dppf$	$BrCH_2CH_2Br$	95	<5
7	$1/2[RhCl(cod)]_2/dppp$	$BrCH_2CH_2Br$	44	36
8	$CoCl_2/3PPh_3$	$BrCH_2CH_2Br$	30	36
9	$^1/_2[RhCl(cod)]_2/dppf$	O_2	11	65
10	$^1/_2[RhCl(cod)]_2/dppf$	$CuCl_2$	11	<5
11	$^1/_2[RhCl(cod)]_2/dppf$	$Cu(OAc)_2$	7	11
12	$^1/_2[RhCl(cod)]_2/dppf$	$ClCH_2CH_2Cl$	15	<5
13[c]	$^1/_2[RhCl(cod)]_2/dppf$	$BrCH_2CH_2Br$	87	<5
14[d]	$^1/_2[RhCl(cod)]_2/dppf$	$BrCH_2CH_2Br$	82	<5
15[e]	$^1/_2$[RhCl(cod)]2/dppf	BrCH2CH2Br	5	<5
16[f]	$^1/_2[RhCl(cod)]_2/dppf$	$BrCH_2CH_2Br$	11	<5
17[g]	$^1/_2[RhCl(cod)]_2/dppf$	$BrCH_2CH_2Br$	20	11

[a] **1a** (0.4 mmol), oxidant (0.8 mmol), catalyst (0.04 mmol), CO (1 atm), and THF (0.45 mL) were used for all entries, except for entry 9 (1 atm oxidant) and entries 14−17 (0.02 mmol catalyst). [b] GLC yield. [c] The amount of catalyst was reduced to 0.008 mmol. [d] The amount of oxidant was reduced to 0.48 mmol. [e] $PhB(OH)_2$ and CsF (0.4 mmol) were used in place of **1a**. [f] Ph_4Sn was used in place of **1a**. [g] PhMgBr was used in place of **1a**.

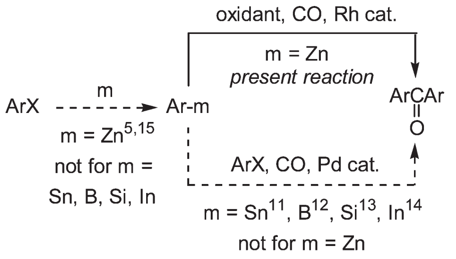
Table 2. Rh-Catalyzed Synthesis of Symmetrical Ketones[a]



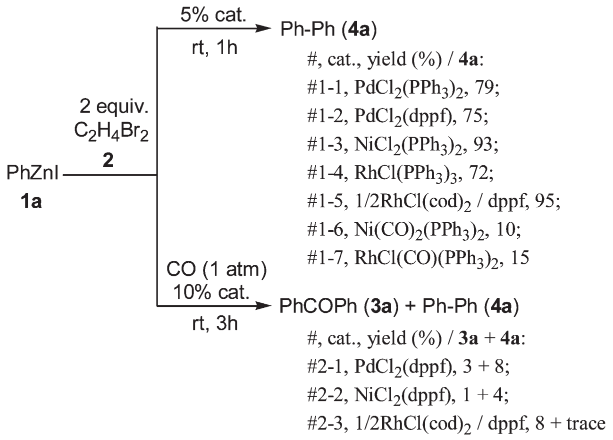
entry	RZnI	product	yield[b] (%)
1	**1a** (R = C_6H_5)	**3a**	79
2	**1b** (R = *p*-NCC_6H_4)	**3b**	93
3	**1c** (R = *p*-$EtO_2CC_6H_4$)	**3c**	74
4	**1d** (R = *p*-BrC_6H_4)	**3d**	84
5	**1e** (R = *o*-BrC_6H_4)	**3e**	88
6	**1f**(R = *p*-$MeOC_6H_4$)	**3f**	95
7	**1g** (R = *p*-MeC_6H_4)	**3g**	78
8	**1h** (R = *m*-MeC_6H_4)	**3h**	91
9	**1i** (R = 2-C_4H_3S)	**3i**	97

[a] RZnI (0.8 mmol), $BrCH_2CH_2Br$ (1.6 mmol), catalyst (0.04 mmol), CO (1 atm), and THF (0.9 mL) were used for all entries. [b] Isolated yield.

Scheme 2. Symmetrical Diaryl Ketones from Aryl Halides



Scheme 3. Effect of CO on the Reaction between 1a and 2

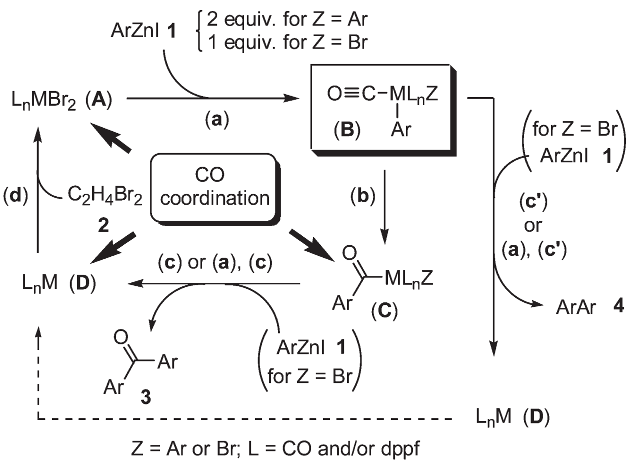


to Ar-m where m = Sn,[11] B,[12] Si,[13] or In,[14] **1** (m = Zn) is the only Ar-m to be available for direct reaction between aryl halides and metallic species,[5,15] while it is not available for carbonylative cross-coupling with ArX (Scheme 2).[1] Therefore, the present reaction provides the most convenient and efficient route to symmetrical diaryl ketones from aryl halides.[16]

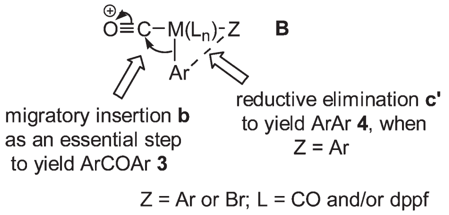
A detailed mechanism remains to be clarified. However, any mechanism must take into account the reason for the superiority of Rh as a catalyst compared to Pd or Ni, in view of the well-known efficiency of the latter in similar carbonylative cross-coupling to yield ketones,[1,11−14,17] as well as oxidative homocoupling to yield biaryls.[18] The catalytic activity of several complexes was examined in the reaction of **1a** with **2** under N_2 in stead of CO atmosphere (Scheme 3). In every run, undertaken at room temperature for 1 h, **4a** was obtained in high yield (1-1−1-5), revealing that all metals examined (Pd, Ni, and Rh[19]) exhibited excellent catalytic activity toward oxidative homocoupling using **1** and **2** as the reaction components. This result is rather surprising, because, in previous runs, Pd or Ni catalysts required much harsher condition (60 °C, for 3 h) to go to completion (Table 1). In fact, under the usual CO atmosphere, oxidative homocoupling proceeded far more slowly at room temperature (2-1 and 2-2). With the Rh catalyst, CO caused an enormous decrease in catalytic activity toward oxidative homocoupling, and while CO insertion occurred primarily, it was quite slow (2-3). Thus, the activity of all catalysts toward oxidative homocoupling was decreased by CO, presumably due to coordination to the metal center. This view might be supported by the inferiority of carbonyl catalysts, $Ni(CO)_2(PPh_3)_2$ or $RhCl(CO)(PPh_3)_2$, in oxidative homocoupling (1-6 and 1-7[20]).

A plausible reaction path of carbonylative, oxidative homocoupling is depicted in Scheme 4, where two transmetalations (reaction **a**), migratory insertion (reaction **b**), reductive elimination

Scheme 4. Reaction Path



Scheme 5. Migratory Insertion vs. Reductive Elimination at Intermediate B



(reaction **c**), and oxidation of the reduced catalyst (M = Rh(I), Pd^0, or Ni^0) to a higher oxidation state (reaction **d**) are involved.[3b−3d] In addition, coordination of CO may take place at any one of the intermediates, **A**, **C**, or **D**, preceding the migratory insertion to form acylcomplex **C** (Z = Ar or Br). As a side reaction, biaryl formation probably takes place through reaction **a**, followed by another reductive elimination (reaction **c**′) and then reaction **d**, where CO acts as a spectator ligand but affects the activity of the catalyst to yield **4** (Scheme 5). Under slightly forcing conditions (60 °C), Rh catalyst first achieves the formation of **3**, implying that the migratory insertion **b** takes place selectively and rapidly at the key intermediate **B**, followed by reductive elimination **c** to form **3**. This pathway overcomes reductive elimination **c**′ to form **4** from **B** with Z = Ar.[21] In contrast, Pd or Ni catalysts make the migratory insertion **b** less facile than Rh does,[21] and even under CO atmosphere, these catalysts afforded **4** predominantly, via **B** with Z = Ar, although slight heating is required to induce the reaction.

In conclusion, the synthesis of functionalized symmetrical biaryl ketones from readily available arylzinc nucleophiles and CO (1 atm) revealed that only Rh exhibited excellent catalytic activity for the carbonylation. Rh also suppressed the homocoupling of arylzinc compounds with 1,2-dibromoethane as oxidant, which takes place extremely easily, not only by catalysis with Rh but also with Pd or Ni under milder conditions in the absence of CO.

EXPERIMENTAL SECTION

Representative Procedure. The reaction flask containing the solution composed of $[RhCl(cod)]_2$ (9.8 mg, 0.02 mmol), dppf (22.2 mg, 0.04 mmol), and THF (0.10 mL) was purged with CO after being connected with a balloon filled with CO. The solution was stirred for 10 min at ambient temperature before 0.73 mL of 1.1 mol/L THF solution of 4-cyanophenylzinc iodide **1b** (0.80 mmol) and 1,2-dibromoethane **2** (0.066 mL, 0.80 mmol) were added successively and stirred at 60 °C for 3 h. After the successive treatment of the resulting mixture with aqueous HCl and brine, the ether extract was chromatographed on a silica gel column, affording 86.3 mg of 4,4′-dicyanobenzophenone **3b** (93%): white solid; mp 157−159 °C (lit.[22] mp 159.5−160 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, 4H, J = 8.7 Hz), 7.88 (d, 4H, J = 8.7 Hz); ^{13}C NMR (75.7 MHz, $CDCl_3$) δ 116.5, 117.7, 130.2, 132.4, 139.7, 193.4.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** General method, compound characterization data, and copies of the ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Another synthetic method of symmetrical diaryl ketones from Ar-m (m = Hg,[3a,16a] Bi,[16b] Sn,[3b] Pb,[16c] or B[16d,16e]) and CO without oxidants is known, where Ar-m oxidatively adds to catalysts. Compared to the harshness of the conditions,[3a,16a] toxicity,[3a,3b16a16c] and/or availability[3a3b16a−16e] of starting materials in comparison with m = Zn, and the low to moderate yields of products reported,[3a3b16b,16d,16e] our method is far more useful.(a) Larock, R. C.; Hershberger, S. A. *J. Org. Chem.* **1980**, *45*, 3840–3846. (b) Cho, C. S.; Yoshimori, Y.; Uemura, S. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 950–957. (c) Kang, S.-K.; Ryu, H.-C.; Choi, S.-C. *Synth. Commun.* **2001**, *31*, 1035–1039. (d) Ohe, T.; Ohe, K.; Uemura, S.; Sugita, N. *J. Organomet. Chem.* **1988**, *344*, C5–C7. (e) Cho, C. S.; Ohe, T.; Uemura, S. *J. Organomet. Chem.* **1995**, *496*, 221–226.

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(19) Under conditions similar to those of runs 1−5, functionalized **1**, e.g., **1c** or **1f**, took part in the reaction to yield the corresponding biaryls in 82% or 97% yields, respectively. Recently, Rh-catalyzed oxidative homocoupling of arylmetallic nucleophiles was reported for the first time, using arylboronic acids and 2,2,6,6-tetramethylpiperidine-*N*-oxyl radical as the nucleophile and oxidant, respectively. See: Vogler, T.; Studer, A. *Adv. Synth. Catal.* **2008**, *350*, 1963–1967.

(20) In the reaction solution of runs 1−7, **3a** was not detected.

(21) At present, it is not clear which property of the catalyst is most critical for facilitating the migratory insertion in the reported reaction. In general, the rate is supposed to tend to increase as the positive charge on the carbonyl carbon increases. See, for example: Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 5th ed.; Wiley-Interscience: New York, 2009; p 182. DFT calculations on model compounds showed that the value becomes highest with the Rh^{3+} intermediate: $(CH_3)_3Rh(CO)$, 0.596; $(CH_3)_2Pd(CO)$, 0.543; $(CH_3)_2Ni(CO)$, 0.543; $CH_3Rh(CO)$; 0.382.

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