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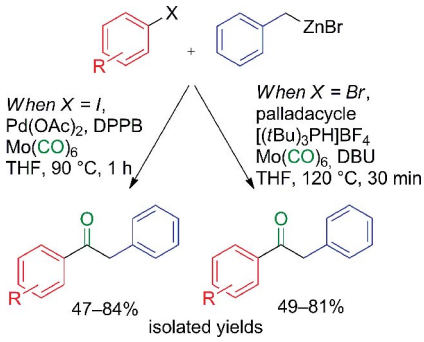
SHORT COMMUNICATION

Carbonylative Cross-Coupling

Two palladium-catalysed gas-free carbonylative Negishi cross-coupling protocols using $Mo(CO)_6$ and microwave irradiation were optimized and used to synthesize a series of diarylated ethanones.



H. V. Motwani, M. Larhed* 1–6

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Diarylated Ethanones from $Mo(CO)_6$-Mediated and Microwave-Assisted Palladium-Catalysed Carbonylative Negishi Cross-Couplings

Hitesh V. Motwani[a] and Mats Larhed*[a]

Keywords: Carbonylation / Cross-coupling / Palladium / Homogeneous catalysis / Metal carbonyls / Microwave chemistry

Two protocols for palladium-catalysed carbonylative Negishi cross-couplings were developed for aryl iodides and aryl bromides. The two main breakthroughs were that molybdenum hexacarbonyl [$Mo(CO)_6$] could be used as a solid in situ source of CO, and that controlled microwave irraditaion could be used for heating. Consequently, the reactions were safe (in contrast to when CO gas was used) and fast (in comparison to when conventional heating was used). The carbonylative cross-coupling reactions were carried out using commercially available benzylzinc bromide in closed vials (90–120 °C for 0.5–1 h) to give a set of diarylated ethanones, a common pharmacophore found in several pharmaceuticals, in moderate to high isolated yields (47–84 %). The mild three-component carbonylation protocol presented here is operationally simple, safe, and rapid, and the formation of the carbonylative Negishi cross-coupling product is favoured over the product of Negishi cross-coupling.

Introduction

In the drug discovery process, it is common practice to synthesize series of congeners based on pharmacophore templates to explore structure–activity relationships for the targets of interest. For this purpose it is important to have access to rapid, robust, and reliable synthetic methods. The 1,2-diarylated ethanone (deoxybenzoin) structure is a common pharmacophore that is found in several pharmaceuticals. Examples of drugs that contain a 1,2-diarylated ethanone substructure include Bermoprofen (anti-inflammatory), Oxacarbazepine (anti-convulsant) and Narceine (analgesics).[1–3] Palladium-catalysed Heck, Stille, and Negishi reaction protocols have been developed for the synthesis of various deoxybenzoins, both by our group and others.[4–7] The carbonylative Negishi cross-coupling (Scheme 1) is a less explored method for the functionalization of aryl halides.[8] An important synthetic advantage of the Negishi carbonylation reaction is that organozinc compounds, which are widely available with different substituents, are less toxic than, for example, organostannanes.[5]

All examples of the palladium-catalysed carbonylative Negishi couplings reported in the literature use CO gas to carry out the carbonylation, and the reaction time required is of the order of many hours (ca. 20–30 h).[6,9–12] CO is a highly poisonous gas, mainly due to its ability to bind to haemoglobin and inhibit the transport of oxygen from the lungs. Furthermore, the gas is odourless, invisible, and flammable. To enable safe handling of CO in a standard laboratory environment, highly specialized equipment that is capable of withstanding elevated pressure is required. Thus, the development of safer and more convenient sources of CO for use in organic synthesis, from which the CO is released in situ, has gained considerable interest over the past few years. For example, several groups have developed different CO-releasing reagents such as chloroform,[13,14] formic acid derivatives,[13,15] aldehydes,[13,16] and acid halides.[17,18] However, following the early report by Corey and Hegedus on the use of the hazardous and volatile $Ni(CO)_4$ in the aminocarbonylation reactions of vinyl bromides,[19] safer metal carbonyls, such as $Mo(CO)_6$ (which contains 6 equiv. of CO), have been tested as solid sources of CO in various palladium-catalysed carbonylation reactions.[20–23] In this paper, we have applied $Mo(CO)_6$-assisted carbonylation to palladium-catalysed Negishi cross-coupling reactions for the first time. Furthermore, to the best of our knowledge, microwave heating has not been used before in carbonylative Negishi couplings. A dedicated single-mode microwave reactor offers advantages over

Scheme 1. Negishi cross-coupling vs. carbonylative Negishi cross-coupling.

[a] Organic Pharmaceutical Chemistry, Department of Medicinal Chemistry, Uppsala Biomedical Centre, Uppsala University, Box 574, 75123 Uppsala, Sweden
E-mail: mats@orgfarm.uu.se
Homepage: http://www.orgfarm.uu.se

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traditional heating methods, including operational safety, and shorter reaction times.[23] In addition, microwave heating gives a high degree of control over the reaction, and offers the possibility of easily changing the temperature on the fly.[24,25] We report the development of two efficient palladium-catalysed carbonylative Negishi cross-coupling protocols using aryl iodides and aryl bromides, respectively, to rapidly produce a series of diarylated ethanones. The novelty of these methods comes from the use of $Mo(CO)_6$ as the in situ source of CO, and the use of microwave heating for palladium-catalysed Negishi cross-coupling reactions.

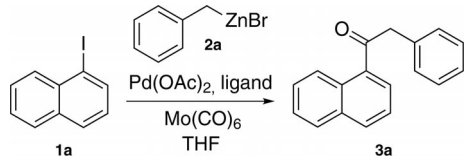
Results and Discussion

Optimization for Aryl Iodides

We began our investigation by using 1-iodonaphthalene (**1a**) as a model aryl iodide, and studying its reaction with benzylzinc bromide (**2a**). Various reaction conditions investigated are shown in Table 1. Using a slight excess of **2a** (1.4 equiv.), a series of experiments were conducted in which the ligand, concentration of $Mo(CO)_6$, temperature, and microwave heating time were varied. Benzylzinc bromide was obtained commercially as a solution (0.5 M) in THF, hence THF was chosen as the solvent. Various ligands were tested {DPPB [1,4-bis(diphenylphosphino)butane], DPPP [1,3-bis(diphenylphosphino)propane], X-phos [2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl], Xantphos [4,5-bis(diphenylphosphino)-9,9-dimethylxanthene]; Table 1, entries 1, 6, 7, and 8, respectively}, and the best yield was obtained with DPPB (76%; Table 1, entry 1). The use of a base, e.g., DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), Et_3N, or K_2CO_3 (Table 1, entries 3, 4, and 5, respectively), was found to be detrimental (yields 69, 33, and 22%, respectively).

When $Pd(OAc)_2$ (10 mol-%) and DPPB (10 mol-%) were used as the palladium catalyst and ligand, respectively, with $Mo(CO)_6$ (2 equiv.) under microwave irradiation at 90 °C for 1 h, a 76% yield of deoxybenzoin **3a** was obtained (Table 1, entry 1). The carbonylative cross-coupling dominated over the competing Negishi-coupling product in a ratio of ca. 9:1 (cf. Scheme 1). The yield decreased compared to that obtained in Table 1, entry 1 when the catalyst loading was reduced to 5 mol-% (Table 1, entry 2), the amount of $Mo(CO)_6$ was reduced to 1 equiv. (Table 1, entry 12), the heating time was reduced to 30 min (Table 1, entry 9), or the temperature was reduced to 70 °C (Table 1, entry 10). When the temperature was increased to 110 °C (Table 1, entry 11), a yield similar to that achieved at 90 °C (Table 1, entry 1) was obtained. When the reaction was performed in the absence of a palladium source and a ligand, less than 5% of product **3a** was detected.[26] When the amount of $Mo(CO)_6$ was reduced to 1 equiv., but the temperature was increased to 110 °C (Table 1, entry 13) or the reaction time to 120 min (Table 1, entry 14), the yields were not higher than that obtained in Table 1, entry 1. Furthermore, when a reaction was carried out under the conditions of Table 1, entry 1 but with heating to 90 °C in an oil bath (instead of microwave heating), the reaction time was nearly 8 h, and the isolated yield of compound **3a** was similar (75%), demonstrating the advantage of microwave heating in giving a shorter reaction time (1 h).

Table 1. Optimization of reaction conditions for the palladium-catalysed carbonylative Negishi cross-coupling using 1-iodonaphthalene.[a]



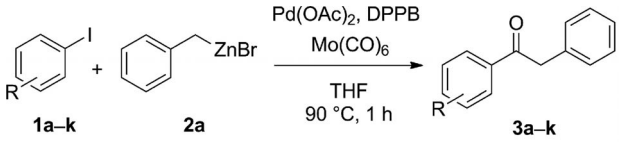
Entry	Ligand	$Mo(CO)_6$ [equiv.]	Temp. [°C]	Time [min]	Yield[f] [%]
1	DPPB	2	90	60	76
2[b]	DPPB	2	90	60	54
3[c]	DPPB	2	90	60	69
4[d]	DPPB	2	90	60	33
5[e]	DPPB	2	90	60	22
6	DPPP	2	90	60	53
7	X-phos	2	90	60	27
8	Xantphos	2	90	60	31
9	DPPB	2	90	30	62
10	DPPB	2	70	60	61
11	DPPB	2	110	60	73
12	DPPB	1	90	60	51
13	DPPB	1	110	60	59
14	DPPB	1	90	120	62

[a] Reactions were performed under microwave irradiation in a sealed vial with **1a** (1 mmol), **2a** (1.4 equiv.), $Pd(OAc)_2$ (10 mol-%), ligand (10 mol-%), and THF (4 mL), unless otherwise specified. [b] Reaction was performed with 5 mol-% $Pd(OAc)_2$. [c] Reaction was performed in the presence of base DBU (2 equiv.). [d] Reaction was performed in the presence of base Et_3N (2 equiv.). [e] Reaction was performed in the presence of base K_2CO_3 (2 equiv.). [f] Isolated yields.

Diarylated Ethanones from Aryl Iodides

Next, we investigated the scope and limitations of the optimized protocol for aryl iodides using benzylzinc bromide. All the reactions shown in Table 2 proceeded under microwave irradiation using a standard single-mode reactor with 1 h of microwave heating; more than 95% conversion of **1a**–**k** was seen, and moderate to good isolated yields (47–84%) of the corresponding 1,2-diarylethanones (i.e., **3a**–**k**) products were obtained. 3-Iodothiophene, as a representative example of a heteroarene, gave 61% of the desired ketone (i.e., **3j**). When 4-cyanobenzylzinc bromide (**2b**) was used instead of **2a** for the reaction with **1a**, product **3k** was obtained in moderate yield (66%), suggesting that the reaction protocol could also be used for substituted benzylzinc bromides. However, further experiments are needed to confirm that various substituted benzylzinc bromides may be used in this protocol.

Table 2. Palladium-catalysed carbonylative Negishi cross-coupling using aryl iodides.[a]



Aryl = 1-naphthyl (**3a**): 76%	R = 4-Me (**3b**): 81%
R = 2-Me (**3c**): 47%	R = 4-CF_3 (**3d**): 56%
R = 4-$CH(Me)_2$ (**3e**): 77%	R = 3-OCH_3 (**3f**): 68%
R = 4-OH (**3g**): 55%	R = 4-OCH_3 (**3h**): 84%
R = 4-CN (**3i**): 73%	
3j: 61%	Aryl = 1-naphthyl (**3k**)[b]: 66%

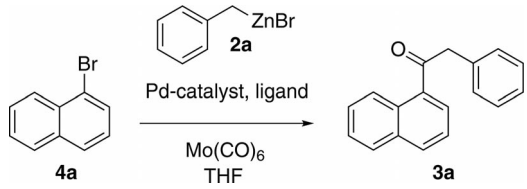
[a] Reactions were performed in a sealed vial with aryl iodides **1a–k** (1 mmol), **2a** (1.4 equiv.), $Mo(CO)_6$ (2 equiv.), $Pd(OAc)_2$ (10 mol-%), DPPB (10 mol-%), and THF (4 mL) under microwave irradiation, unless otherwise specified. [b] 4-Cyanobenzylzinc bromide (**2b**; 1.4 equiv.) was used instead of **2a**.

Optimization for Aryl Bromides

Encouraged by the results obtained with aryl iodides, we decided to extend the scope of our investigation by testing aryl bromides **4** as arylpalladium precursors. This would improve the method as aryl bromides tend to have lower cost than the corresponding iodides, and also more aryl bromides are commercially available. Aryl bromides are less prone to undergo oxidative additions than iodides, so when reaction conditions similar to those used for the aryl iodides were tested with the bromides, the reaction did not proceed as expected, and only a low conversion was observed (12% yield; Table 3, entry 1). Changing the ligand {X-phos, Xantphos, $[(t\text{Bu})_3\text{PH}]\text{BF}_4$} did not improve the yield substantially (14–23%; Table 3, entries 2–4).

We envisaged that a more reactive catalytic system and a higher reaction temperature would allow the transformation to proceed efficiently. This led us to use Herrmann's palladacycle as the palladium source to promote the reactions.[27] The palladacycle was tested with the various ligands (Table 3, entries 5–9), and the best yield was obtained with $[(t\text{Bu})_3\text{PH}]\text{BF}_4$ (61%; Table 3, entry 9). In an attempt to further improve the yield, the reaction was tested in the presence of a base, e.g., DBU, Et_3N, or K_2CO_3 (Table 3, entries 10, 12, and 13, respectively). It was found that, in contrast to the situation with aryl iodides, a base (DBU) improved the efficiency of the reactions of the aryl bromides. The highest yield of **3a** was obtained using Herrmann's palladacycle (5 mol-%) and $[(t\text{Bu})_3\text{PH}]\text{BF}_4$ (10 mol-%) after 30 min of microwave irradiation at 120 °C, with DBU as the base (74%; Table 3, entry 10). Attempts to reduce the reaction time to 15 min (Table 3, entry 11), or the amount of $Mo(CO)_6$ to 1 equiv. (Table 3, entry 14) led to lower yields. When the reaction conditions from Table 3, entry 10 were used with 1-chloronaphthalene and 4-chlorobenzonitrile as substrates, the yields of **3a** and **3i**, respectively, were very low (5–7%), which suggests that this protocol requires further optimization before aryl chlorides can be used as reaction partners.

Table 3. Optimization of reaction conditions for the palladium-catalysed carbonylative Negishi cross-coupling using 1-bromonaphthalene.[a]



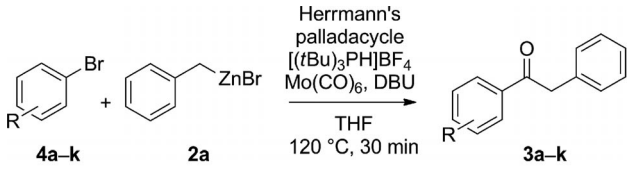
Entry	Pd catalyst	Ligand	Time [min]	Temp. [°C]	Yield[g] [%]
1	$Pd(OAc)_2$	DPPB	60	90	12
2	$Pd(OAc)_2$	X-phos	60	90	14
3	$Pd(OAc)_2$	Xantphos	60	90	17
4	$Pd(OAc)_2$	$[(t\text{Bu})_3\text{PH}]\text{BF}_4$	60	90	23
5	palladacycle	DPPB	30	120	21
6	palladacycle	X-phos	30	120	34
7	palladacycle	Xantphos	30	120	39
8	palladacycle	$[(t\text{Bu})_3\text{PH}]\text{BF}_4$	30	120	49
9[b]	palladacycle	$[(t\text{Bu})_3\text{PH}]\text{BF}_4$	30	120	61
10[c]	palladacycle	$[(t\text{Bu})_3\text{PH}]\text{BF}_4$	30	120	74
11[c]	palladacycle	$[(t\text{Bu})_3\text{PH}]\text{BF}_4$	15	120	57
12[d]	palladacycle	$[(t\text{Bu})_3\text{PH}]\text{BF}_4$	30	120	38
13[e]	palladacycle	$[(t\text{Bu})_3\text{PH}]\text{BF}_4$	30	120	27
14[f]	palladacycle	$[(t\text{Bu})_3\text{PH}]\text{BF}_4$	30	120	59

[a] Reactions were performed under microwave irradiation in a sealed vial with **4a** (1 mmol), **2a** (1.4 equiv.), palladium source (10 mol-%), ligand (10 mol-%), $Mo(CO)_6$ (2 equiv.), and THF (4 mL), unless otherwise specified. [b] Reaction was performed with Herrmann's palladacycle (5 mol-%). [c] Reaction was performed with Herrmann's palladacycle (5 mol-%) in the presence of base DBU (3 equiv.). [d] Reaction was performed with Herrmann's palladacycle (5 mol-%) in the presence of base Et_3N (3 equiv.). [e] Reaction was performed with Herrmann's palladacycle (5 mol-%) in the presence of base K_2CO_3 (3 equiv.). [f] Reaction was performed with 1 equiv. $Mo(CO)_6$ and 3 equiv. DBU. [g] Isolated yields.

Diarylated Ethanones from Aryl Bromides

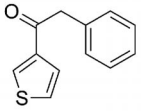
Aryl bromides **4** substituted with different functional groups (Table 4) were found to react under the selected reaction conditions (i.e., Table 3, entry 10) with a similarly high chemoselectivity in favour of carbonylative Negishi cross-coupling to what had been seen with the aryl iodides. However, the conversion of the aryl bromides into the desired product was, in general, not fully complete (ca. 90%). Increasing the reaction time to 1 h (from 30 min) and the temperature to 140 °C (from 120 °C) did not give a substantial increase of the conversion, but resulted instead in the formation of non-carbonylative by-products. This partly explains the somewhat lower yields (49–81%) obtained for the reactions with the aryl bromides (Table 4) compared to those obtained with the aryl iodides (Table 2).

Table 4. Palladium-catalysed carbonylative Negishi cross-coupling using aryl bromides.[a]



4a–k 2a 3a–k

Aryl = 1-naphthyl (**3a**): 74%	R = 4-Me (**3b**): 61%
R = 2-Me (**3c**): 49%	R = 4-CF_3 (**3d**): 53%
R = 4-$CH(Me)_2$ (**3e**): 71%	R = 3-OCH_3 (**3f**): 65%
R = 4-OH (**3g**): 58%	R = 4-OCH_3 (**3h**): 81%
R = 4-CN (**3i**): 66%	



3j: 62% Aryl = 1-naphthyl (**3k**)[b]: 63%

[a] Reactions were performed in a sealed vial with aryl bromides **4a**–**k** (1 mmol), **2a** (1.4 equiv.), $Mo(CO)_6$ (2 equiv.), Herrmann's palladacycle (5 mol-%), $[(tBu)_3PH]BF_4$ (10 mol-%), DBU (3 equiv.), and THF (4 mL) under microwave irradiation, unless otherwise specified. [b] 4-Cyanobenzylzinc bromide (**2b**; 1.4 equiv.) was used instead of **2a**.

Conclusions

New, convenient and efficient palladium-catalysed carbonylative Negishi cross-coupling protocols have been developed. Aryl halides (iodides or bromides) are treated with benzylzinc bromide in the presence of $Mo(CO)_6$ under microwave heating. A broad array of diarylated ethanones were produced with high chemoselectivity and in moderate to high (47–84%) isolated yields using these single-vial methods optimized for either aryl iodides or aryl bromides. To the best of our knowledge, this is the first report to present carbonylative Negishi cross-coupling reactions in which a solid CO source has been used. In comparison to classical carbonylative Negishi cross-coupling reactions that use CO gas, the use of a solid CO source [$Mo(CO)_6$] is safer, easier, and faster. Furthermore, the rate of the reactions was significantly enhanced by using microwave irradiation for heating. In view of the short reaction times and the robustness of the methods, we anticipate that our work will facilitate the preparation of diarylated ethanone derivatives for various future medicinal-chemistry-related applications.

Experimental Section

Caution: Pressurized carbonylation reactions should be carried out using appropriate and safe equipment, such as the microwave reactor used in this study. CO is a poisonous gas, so all reactions involving CO should be carried out in well-ventilated fume hoods, preferably with a CO detector to warn of any exposure.

The compounds synthesized were: 1-(naphthalen-1-yl)-2-phenylethanone (**3a**);[28] 2-phenyl-1-(*p*-tolyl)ethanone (**3b**);[28,29] 2-phenyl-1-(*o*-tolyl)ethanone (**3c**);[29] 2-phenyl-1-[4-(trifluoromethyl)phenyl]-ethanone (**3d**);[30,31] 1-(4-isopropylphenyl)-2-phenylethanone (**3e**);[32,33] 1-(3-methoxyphenyl)-2-phenylethanone (**3f**);[29] 1-(4-hydroxyphenyl)-2-phenylethanone (**3g**);[34] 1-(4-methoxyphenyl)-2-phenylethanone (**3h**);[28,29] 4-(2-phenylacetyl)benzonitrile (**3i**);[31] 2-phenyl-1-(thiophen-3-yl)ethanone (**3j**);[6] and 4-[2-(naphthalen-1-yl)-2-oxoethyl]benzonitrile (**3k**).[35] Yields are given in Tables 2 and 4.

Supporting Information (see footnote on the first page of this article): Experimental details, ^1H and ^{13}C NMR spectra, and chromatograms for all products.

Acknowledgments

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