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First Kumada reaction of alkyl chlorides using *N*-heterocyclic carbene/palladium catalyst systems

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Dedicated to Prof. Jean-Pierre Genêt on the occasion of his 60th birthday

Abstract

For the first time it is shown that *N*-heterocyclic carbenes are suitable ligands for the palladium-catalyzed coupling of alkyl chlorides with aryl Grignard reagents. A variety of simple as well as functionalized primary alkyl chlorides provide the corresponding alkyl benzenes in general in good to very good yield. By comparing the 1,3-dimesitylimidazol-2-ylidene (IMes) palladium(0) naphthoquinone complex with the previously known palladium phosphine catalyst for the model coupling reaction of 1-chlorohexane with phenylmagnesium bromide it is demonstrated that the new catalyst system is superior.

Keywords: *N*-heterocyclic carbenes; Palladium-catalyzed coupling; Alkyl chlorides

1. Introduction

Organometallic cross coupling reactions have proven to be extremely important for the synthesis of organic building blocks, pharmaceuticals and agrochemicals in derivatives in recent years. In this area, aryl and vinyl chlorides are among the most useful starting materials due to their low cost and easy availability, which allows not only laboratory-scale syntheses but also industrial applications [1]. Activation of C–Cl bonds and subsequent C–C coupling reactions are generally performed using simple olefins, organoboronic or organomagnesium derivatives (Heck, Suzuki and Kumada reactions, respectively). Important contributions have been made in the last decade on this topic of current interest [2–8].

Palladium-catalyzed coupling reactions of alkyl chlorides ($C(sp^3)$–Cl bonds) have been much less studied so far. There are mainly two reasons, which explain the difficulty of this catalytic transformation: (i) the slow oxidative addition of the alkyl chloride to the palladium; and (ii) the ease of β-hydride elimination reactions of the palladium alkyl complexes in cases where the oxidative addition has taken place. Nevertheless, already in the early to mid 1990s Suzuki et al. [9] and Knochel et al. [10] have demonstrated the possibility of palladium- and nickel-catalyzed coupling of alkyl bromides with alkyl boranes as well as with organozinc derivatives. We were also able to show that palladium-catalyzed carbonylations of in situ generated α-amidoalkyl bromides proceed in good yields to the corresponding amino acid derivatives [11].

More recently, the first general method for catalytic coupling reactions of alkyl halides was described by Fu et al. [12] who performed palladium-catalyzed Suzuki reactions, whereas Kambe et al. [13] reported on the efficient nickel-catalyzed Kumada coupling of 1-chlorooctane with *n*-butylmagnesium chloride in the presence of 50 mol% of 1,3-butadiene. Our group has recently reported the first palladium-catalyzed Kumada reaction using tricyclohexylphosphine as ligand, which allows the room-temperature coupling of various aryl magnesium bromides with several functionalized and non-functionalized alkyl chlorides [14].

In the last decade *N*-heterocyclic carbenes have been shown to be alternative ligands to organophosphines for organometallic and inorganic coordination chemistry.

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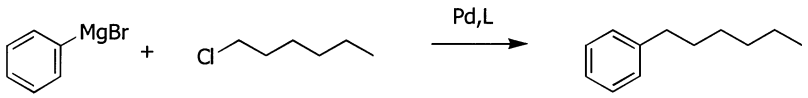
Table 1



Entry	[Pd]	Ligand	Pd: L	Conv. [%][a]	Yield [%][a]
1	IMesPd(dvds)	-		2	2
2	IPrPd(dvds)	-		1	1
3	IMesPd(NQ)	-		99	98
4	IPrPd(NQ)	-		81	51
5	$Pd(OAc)_2$	IMesHCl	1.1	89	75
6	$Pd(OAc)_2$	IMesHCl	1.2	36	15
7	$Pd(OAc)_2$	IPrHCl	1.1	74	14
8	$Pd(OAc)_2$	IPrHCl	1.2	54	17

2 mmol alkyl chloride, 3 mmol PhMgBr (1M in THF), 4 mol% Pd, 5 mL NMP, 1 h, RT. [a] determined by GC using diethyleneglycol di-n-butyl ether as internal standard.

Thus, palladium carbene complexes have become increasingly important as catalysts for Heck, Suzuki and Sonogashira coupling reactions, copolymerizations and amination of aryl halides [15]. However, to the best of our knowledge, no example of catalytic coupling reactions with alkyl halides using *N*-heterocyclic carbenes as ligands has been reported until now. Here, we wish to describe the first successful development of such a palladium-catalyzed method in the Kumada cross-coupling reaction of alkyl chlorides.

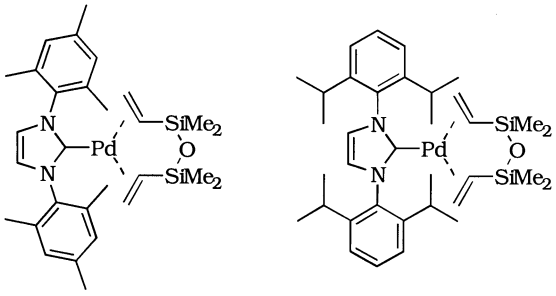


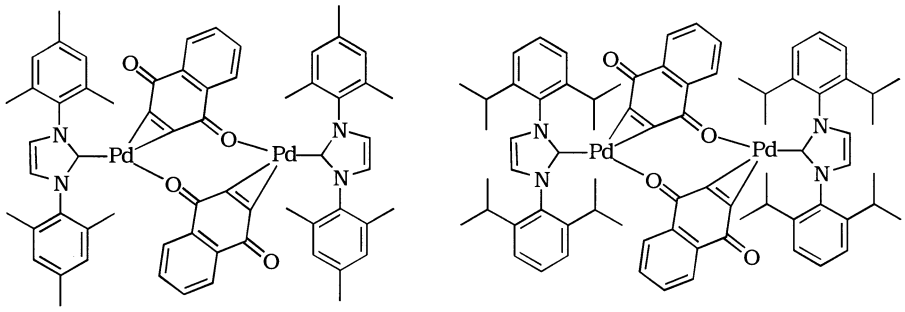
Fig. 1. Carbene palladium dvds complexes (dvds = 1,1,3,3-tetramethyl-1,3-divinyl-1,3-disiloxane).

2. Results and discussion

During our ongoing efforts to develop novel molecularly defined palladium(0) (pre)catalysts for C–C coupling reactions we found that carbene-palladium(0) diene complexes such as **1** and **2** are excellent catalysts for the telomerization reaction of 1,3-butadiene with alcohols [16].

Carbene-palladium(0) quinone complexes **3** and **4** were found to be suitable as catalysts for Heck and Suzuki reactions of aryl chlorides and aryl diazonium salts [17].

After having demonstrated the general possibility of palladium-catalyzed coupling reactions of alkyl chlorides with Grignard reagents in the presence of PCy_3 [14], we wondered whether other ligands were also suited for this reaction. However, a screening of different sterically hindered alkyl and aryl phosphines in our test reaction of 1-hexyl chloride and phenylmagnesium bromide did not lead to any improvement. On the other hand we were surprised to find that palladium carbene complexes catalyze this coupling process. While both dvds complexes (dvds = 1,1,3,3-tetramethyl-1,3-divinyl-1,3-disiloxane) are almost inactive (Table 1, entries 1 and 2), the corresponding naphthoquinone complexes give the desired product in moderate to excellent yield in the test reaction (Table 1, entries 3 and 4) (Figs. 1 and 2). These experiments show for the first time that *N*-heterocyclic carbenes are suitable ligands for palladium-catalyzed coupling reactions of alkyl chlorides. It is worth



3 4

Fig. 2. Carbene palladium naphthoquinone complexes.

mentioning that the activity of complex **3** is higher than that of the previously known palladium/PCy_3 system. While the optimized palladium phosphine catalyst needed 16 h for complete conversion at room temperature, the monocarbene–palladium catalyst **3** leads to full conversion within 1 h.

The difference of reactivity of the dvds and naphthoquinone complexes is explained by the stronger binding of dvds to the palladium center, which is thus blocking the free coordination sites of the monocarbene–palladium(0) fragment under our mild reaction conditions (room temperature). Quinones, in contrast, might be attacked by the Grignard reagent, liberating the highly reactive monocarbene–palladium(0) unit. Unfortunately, we have not been able to detect naphthoquinone or an addition product with the Grignard reagent after the reaction has been completed.

Also in situ mixtures of imidazolium salts and palladium(II) acetate do lead to active catalysts (Table 1, entries 5–8). However, the in situ catalysts show a somewhat lower activity compared to the defined monocarbene–palladium(0) complex. Interestingly, only a 1:1 mixture of 1,3-dimesitylimidazolium hydrochloride (IMesHCl) and $Pd(OAc)_2$ gives a considerable yield of coupling product. Higher concentration of the imidazolium salt leads to catalyst deactivation (Table 1, entries 5 and 6), hence demonstrating the importance of free coordination sites on the palladium center. A comparison experiment of 1,3-dimesitylimidazolium hydrochloride (IMesHCl) and 1,3-(2,6-diisopropylphenyl)imidazolium hydrochloride (IPrHCl) (Table 1, entries 5 and 7) showed that IMes is a more suitable ligand than the sterically more demanding IPr.

Next, complex **3** was used for further experiments, demonstrating the generality of the new catalyst system (Table 2). Simple alkyl chlorides are coupled easily with substituted and non-substituted aryl Grignard reagents (Table 2, entries 1–4, 7 and 8). *Ortho*-substitutents on the arene are tolerated to some extent (Table 2, entries 5 and 6). Arylalkyl chlorides can also be reacted under standard conditions, leading to good yields (Table 2, entry 9). Unfortunately, secondary alkyl chlorides like cyclohexyl or *i*-propyl chloride could not be coupled with synthetically useful yields so far.

Because of the mild reaction conditions and fast reaction rates for the desired coupling, functionalities which are often incompatible with Grignard reagents are tolerated by our system. Nitrile and ester groups are not attacked to a significant amount (Table 2, entries 10 and 11), but the cyclic imide unit in *N*-(chloroalkyl)phthalimide leads to some side products, giving the desired coupling products only in moderate yield (33–45%) (Table 2, entries 12 and 13).

3. Summary and outlook

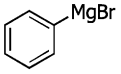
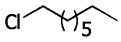
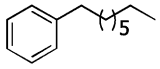
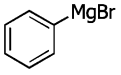
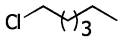
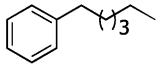
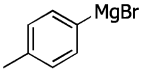
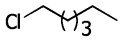
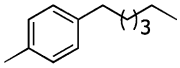
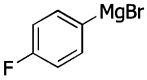
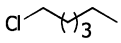
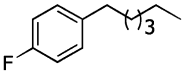
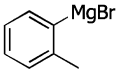
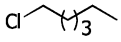
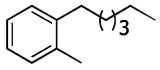
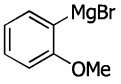
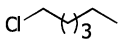
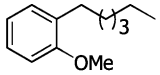
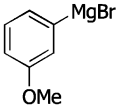
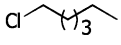
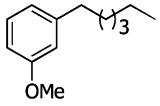
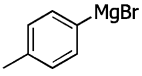
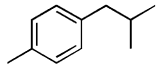
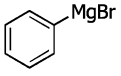
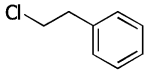
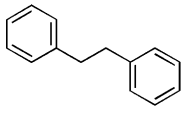
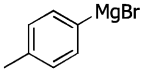
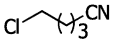
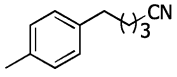
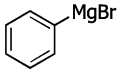
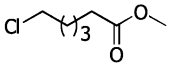
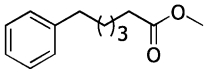
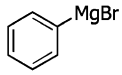
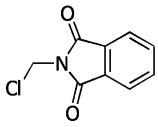
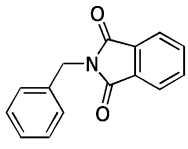
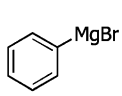
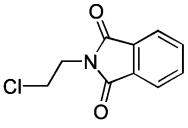
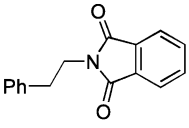
The usefulness of *N*-heterocyclic carbenes as ligands for the palladium-catalyzed coupling of primary alkyl chlorides with arylmagnesium bromides has been demonstrated for the first time. Functional groups on both coupling partners can be tolerated. The defined monocarbene–palladium(0) naphthoquinone complex **3** was found to be the most efficient catalyst for this type of reactions so far. Remarkable are the mild conditions (room temperature) and the fast reaction (< 1 h) of this coupling process. Further investigations using modified carbene ligands for the non-precedented coupling of secondary and tertiary alkyl chlorides are underway in our laboratory.

4. Experimental

4.1. General

All syntheses were carried out using standard Schlenk techniques under an argon atmosphere. All chemicals were used as received from commercial suppliers. IMesHCl, IPrHCl [18] and NHC–palladium complexes [17a,19] were prepared according to literature procedures.

Table 2

Entry	Ar-MgX	Alkyl chloride	Product	Conv. [%][a]	Yield [%][a]
1				100	97
2				96	85
3				100	98
4				100	98
5				100	91
6				99	61
7				99	99
8				100	99
9				99	70
10				100	93
11				100	92
12				100	33
13				99	45

2 mmol alkyl chloride, 3 mmol Ar-MgBr (1M in THF), 2 mol% 3, 5 mL NMP, 1 h, RT. [a] determined by GC using diethyleneglycol di-n-butyl ether as internal standard.

4.2. General procedure for Kumada reactions

A Schlenk flask was charged with a mixture of $Pd(OAc)_2$ (0.018 g, 4 mol%) and imidazolium salt (4 mol%) or with the preformed palladium catalyst (4 mol%), sealed with a septum, and purged with argon. NMP (5 ml) and alkyl chloride (2 mmol) were added by syringe. Then, Ar–MgBr (3 mmol, 3 ml of a 1 M solution in THF) was added dropwise over 1 min to the stirred mixture. After 1 h at room temperature, the reaction was quenched with MeOH (1 ml) and water (1 ml). The product was isolated by column chromatography (silica gel, heptane).

4.3. 1-n-Hexyl-2-methylbenzene

Colorless liquid. IR (KBr): 2956 s, 2928 s, 2858 s, 1605 w, 1493 m, 1460 m, 1378 m, 740 s. MS (EI, 70 eV): 176 ($[M]^+$, 29%), 105 ($[tolCH_2]^+$, 100%), 91 ($[Bn]^+$, 14%), 79 (8%). ^{1}H-NMR (400 MHz, $CDCl_3$): 6.92–6.80 (m, 4H, Ar), 2.34 (t, $J_{HH} = 7.9$ Hz, 2H, Ar–CH_2), 2.06 (s, 3H, Ar–CH_3), 1.39–1.27 (m, 2H, Ar–CH_2–CH_2), 1.15–1.00 (m, 6H, (CH_2)$_3$–CH_3), 0.70–0.63 (m, 3H, CH_2–CH_3). ^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): 141.1, 135.8, 130.1, 128.7, 125.8, 125.7, 33.3, 31.8, 30.3, 29.4, 22.6, 19.3, 14.1. Elemental Anal. Calc. for $C_{13}H_{20}$ (176.3): C, 88.57; H, 11.43. Found: C, 88.60; H, 11.33%.

4.4. 1-Isobutyl-4-methylbenzene

Colorless liquid. MS (EI, 70 eV): 148 ($[M]^+$, 41%), 105 ($[tolCH_2]^+$, 100%), 91 ($[Bn]^+$, 17%), 79 (10%). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.10–7.00 (m, 4H, Ar), 2.43 (d, $^3J_{HH} = 7.1$ Hz, 2H, Ar–CH_2), 2.31 (s, 3H, Ar–CH_3), 1.89–1.77 (m, $^3J_{HH} = 6.8$ Hz, 1H, CH), 0.89 (d, $^3J_{HH} =$ 6.7 Hz, 6H, CH–(CH_3)$_2$). ^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): 138.6, 134.9, 129.0, 128.7, 45.0, 30.3, 22.4, 21.0.

4.5. 1-Fluoro-4-n-hexylbenzene

Colorless liquid. IR (KBr): 2957 s, 2929 s, 2857 s, 1601 w, 1510 s, 1458 w, 1222 s, 1157 m, 824 m. MS (EI, 70 eV): 180 ($[M]^+$, 33%), 109 ($[F–Bn]^+$, 100%); 96 ($[F–Ph]^+H$, 5%). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.16–7.07 (m, 2H, Ar), 7.00–6.90 (m, 2H, Ar), 2.58 (t, $^3J_{HH} = 7.7$ Hz, 2H, Ar–CH_2), 1.65–1.50 (m, 2H, Ar–CH_2–CH_2), 1.38–1.24 (m, 6H, (CH_2)$_3$–CH_3), 0.90 (t, $^3J_{HH} = 6.8$ Hz, 3H, CH_2–CH_3). ^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): 161.1 (d, $^1J_{CF} = 242.2$ Hz), 138.4 (d, $^4J_{CF} = 2.9$ Hz), 129.6 (d, $^3J_{CF} = 7.9$ Hz), 114.9 (d, $^2J_{CF} = 21.0$ Hz), 35.1, 31.7, 31.6, 28.9, 22.6, 14.1. Elemental Anal. Calc. for $C_{12}H_{17}F$ (180.26): C, 79.96; H, 9.51. Found: C, 79.46; H, 9.84%.

4.6. 5-p-Tolylpentanenitrile

Yellow liquid. IR (KBr): 3047 m, 3020 m, 2928 s, 2861 s, 2246 (CN) m, 1515 s, 1458 s, 1425 s, 809 s. MS (EI, 70 eV): 173 ($[M]^+$, 15%), 105 ($[tolCH_2]^+$, 100%), 91 ($[Bn]^+$, 8%), 77 ($[Ph]^+$, 10%). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.09 (d, $^3J_{HH} = 7.9$ Hz, 2H, Ar), 7.04 (d, $^3J_{HH} = 7.9$ Hz, 2H, Ar), 2.60 (t, $^3J_{HH} = 7.3$ Hz, 2H, Ar–CH_2), 2.35–2.29 (m, 5H, Ar–CH_2–CH_2, Ar–CH_3), 1.80–1.60 (m, 4H, CH_2–CH_2–CN). ^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): 138.1, 135.5, 129.1, 128.2, 119.6, 34.5, 30.3, 24.8, 17.0, 21.0. Elemental Anal. Calc. for $C_{12}H_{15}N$ (187.28): C, 83.19; H, 8.73; N, 8.08. Found: C, 83.00; H, 8.52; N, 7.91%.

4.7. 2-n-Hexyl-1-methoxybenzene

Yellow liquid. IR (KBr): 2955 s, 2926 s, 2856 s, 1494 s, 1465 s, 1438 s, 1242 s, 1052 s, 1033 s, 751 s. MS (EI, 70 eV): 192 ($[M]^+$, 21%), 121 ($[MeO–Br]^+$, 100%), 108 ($[MeO–Ph^+]$, 4%), 91 ($[Br]^+$, 51%), 77 ($[Ph]^+$, 7%). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.20–7.10 (m, 2H, Ar), 6.92–6.80 (m, 2H, Ar), 3.82 (s, 3H, OCH_3), 2.61 (t, $^3J_{HH} = 7.8$ Hz, 2H, Ar–CH_2), 1.65–1.52 (m, 2H, Ar–CH_2–CH_2), 1.41–1.20 (m, 6H, (CH_2)$_3$–CH_3), 0.94–0.84 (m, 3H, CH_2–CH_3). ^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): 157.9, 131.8, 130.2, 127.2, 120.7, 110.6, 55.7, 32.2, 30.6, 30.3, 29.8, 23.1, 14.6. Elemental Anal. Calc. for $C_{13}H_{20}O$ (192.30): C, 81.20; H, 10.48. Found: C, 81.47; H, 10.80%.

4.8. 3-n-Hexyl-1-methoxybenzene

Colorless liquid. IR (KBr): 2999 s, 2928 s, 2856 s, 1602 s, 1585 s, 1488 s, 1466 s, 1437 s, 1261 s, 1165 s, 1152 s, 1049 s, 776 s. MS (EI, 70 eV): 192 ($[M]^+$, 22%), 135 (12%), 121 ($[MeO–Br]^+$, 100%), 107 ($[MeO–Ph]^+$, 8%), 91 ($[Br]^+$, 23%), 77 ($[Ph]^+$, 11%). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.15–7.06 (m, 1H, Ar), 6.73–6.60 (m, 3H, Ar), 3.71 (s, 3H, OCH_3), 2.50 (t, $^3J_{HH} = 7.7$ Hz, 2H, Ar–CH_2), 1.59–1.47 (m, 2,H, Ar–CH_2–CH_2), 1.30–1.15 (m, 6H, (CH_2)$_3$–CH_3), 0.86–0.74 (m, 3H, CH_2–CH_3). ^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): 159.6, 144.6, 129.1, 120.8, 114.2, 110.8, 55.1, 36.0, 31.7, 31.4, 29.0, 22.5, 14.1. Elemental Anal. Calc. for $C_{13}H_{20}O$ (192.30): C, 81.20; H, 10.48. Found: C, 81.58; H, 10.57%.

4.9. Methyl 6-phenylhexanoate

Yellow liquid. MS (EI, 70 eV): 206 ($[M]^+$, 4%), 105 ($[Ph–C_2H_4]^+$, 100%), 91 ($[Br]^+$, 14%), 77 ($[Ph]^+$, 11%). ^{1}H-NMR (400 MHz, C_6D_6): 7.17–7.40 (m, 5H, Ar), 4.10 (s, 3H, OCH_3), 2.54 (t, $^3J_{HH} = 7.7$ Hz, 2H, ArCH_2), 1.84 (t, $^3J_{HH} = 6.7$ Hz, 2H, CH_2CO$_2$), 1.25–1.59 (m, 6H, (CH_2-CH_2)$_3$–CH_2). ^{13}C{^{1}H}-NMR (101 MHz, C_6D_6):

170.3 (*C*O), 142.8, 128.9, 128.8, 126.3, 64.5 (O*C*H_3), 36.3, 31.6, 29.0, 26.0, 20.8.

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