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First Heck Reaction with Arenediazonium Cations with Recovery of Pd-Triolefinic Macrocyclic Catalyst

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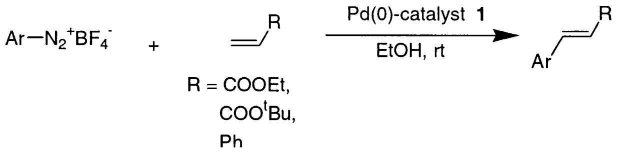
ABSTRACT



The air- and moisture-stable phosphine-free palladium(0) complex 1 is a highly active and recoverable catalyst for Heck olefination of aryl diazonium tetrafluoroborates. The reactions were performed under aerobic conditions at room temperature to give the coupling products in excellent yields.

The palladium(0)-catalyzed reaction of aryl and alkenyl halides with alkenes (the Heck reaction) represents one of the most versatile tools in modern synthetic chemistry and has great potential for industrial applications.[1] In view of the economy of the reaction, the recovery as well as recycling of the expensive palladium catalyst is essential. In general, palladium(0) requires stabilization by phosphines, which are readily oxidized and consequently cause the loss of the catalyst. Therefore, the development of phosphine-free palladium catalysts is a topic of enormous importance.

Recently, we published synthetic procedures for a novel type of palladium(0) complexes of 15-membered macrocyclic triolefins containing different aryl units, for example, the structure **1** represented in Figure 1.[2] These phosphine-free palladium(0) complexes are air- and moisture-stable and recoverable catalysts in Suzuki cross-couplings,[2b] in the telomerization of butadiene,[3] and in the hydroarylation of alkynes in ionic liquids.[4]

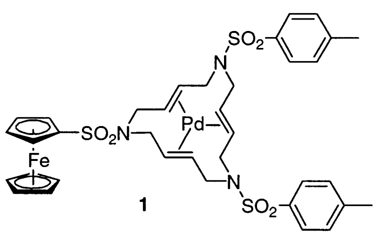


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Figure 1. Structure of Pd(0) catalyst, **1**.

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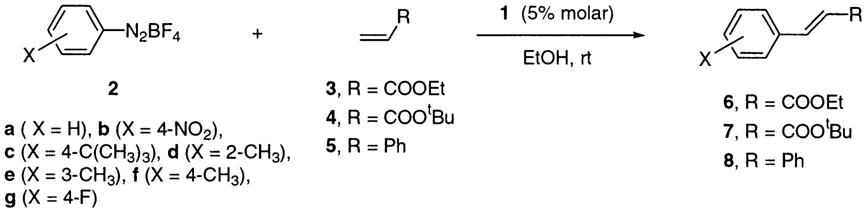
Table 1. Heck Reaction of Arenediazonium Salts **2** Using Pd(0) Complex **1**[a]



entry	diazonium salt, **2**	olefin	time (h)	product	yield[b] (%)	recovery of **1**[b] (%)
1	**2a**	**3**	1.25	**6a**	95	97
2	**2b**	**3**	0.75	**6b**	95	100
3	**2c**	**3**	1	**6c**	100	97
4	**2d**	**3**	1.50	**6d**	100	95
5	**2e**	**3**	1.25	**6e**	78	94
6	**2f**	**3**	0.75	**6f**	97	100
7	**2g**	**3**	0.75	**6g**	78	100
8	**2a**	**4**	3	**7a**	88	99
9	**2b**	**4**	2.75	**7b**	100	99
10	**2c**	**4**	4	**7c**	100	97
11	**2d**	**4**	3.75	**7d**	71	95
12	**2e**	**4**	6.5	**7e**	69	88
13	**2f**	**4**	3	**7f**	99	95
14	**2g**	**4**	2.5	**7g**	94	98
15[c]	**2a**	**5**	4.25	**8a**	97	98
16[d]	**2b**	**5**	3.5	**8b**	100	95
17[c]	**2c**	**5**	4	**8c**	96	95
18[c]	**2d**	**5**	4	**8d**	38	93

[a] Reactions were carried out under aerobic conditions. Molar ratio **2**/olefin ca. 1:1.6, [**2**] ca. 0.023 M. [b] Isolated by column chromatography on silica gel. [c] 10% of catalyst **1** was required. [d] 15% of catalyst **1** was required.

Another drawback in the Heck reaction is the need for high-cost aryl iodides or bromides as the most used aryl electrophile components (ArX). An interesting alternative to aryl halides for Heck reactions has been the use of arenediazonium salts.[5] Diazonium salts offer several advantages over the aryl halides: economic advantage of anilines compared to aryl bromides and iodides, short reaction times, mild and aqueous reaction conditions without added base, and superior reactivity of the diazonium nucleofuge (N_2) over the bromides and iodides.

To the best of our knowledge, there has been no general study of Heck reactions of aryl diazonium salts with recovered catalyst described to date. Thus, we want to present here the efficiency and recovery of palladium(0) complex **1** as catalyst in several Heck reactions summarized in Table 1.

Initial screening of the reaction conditions with the diazonium salt **2a** and ethyl acrylate **3** revealed that the arylation was achieved using 5 mol % of Pd(0) catalyst **1** in ethanolic solution at room temperature. It has to be pointed out that the reaction was practical and very fast under aerobic conditions using commercial and not degassed solvent. Pd(0) complex **1** was almost quantitatively recovered (97%) by column chromatography on silica gel. The synthetic efficacy of this reaction was studied with a number of arenediazonium salts **2a**−**g** and the olefins ethyl acrylate, **3**, *tert*-butyl acrylate, **4**, and styrene, **5**. Table 1 shows that the nature of the substituents did not exert significant effect on the yields and recovery of the catalyst. Formation of nitro-substituted derivatives **6b** (entry 2), **7b** (entry 9), and **8b** (entry 16), from the 4-nitro salt **2b**, are also quite significant since this salt failed in several Heck reactions with acrylates.[5b,e] Surprisingly, 4-methoxydiazonium salt failed to participate in this reaction. Steric effects of ortho or meta substituents do not seem to affect the reactivity of arenediazonium salts (entries 5 and 6 in the case of olefin **3**; entries 12 and 13 in the case of olefin **4**). Only in the case of styrene **5** did steric effects come into play causing lowering of yields (entry 18). In addition, *m*-methylbenzenediazonium tetrafluoroborate **2e**

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is much more sensitive to decomposition than the other isomers, giving lower yields (entries 5 and 12), or failing in the case of styrene. In general, longer reaction times were needed using *tert*-butyl acrylate **4** and styrene **5**. In the case of styrene, using 5% of catalyst, **1,** products were obtained in excellent yields, but longer reaction times were required and the catalyst was recovered only in 85% yield. To improve the recovery of complex **1**, 10% of catalyst was needed (entries 15, 17, and 18).

In the case of diazonium salts in Heck reactions, it has been postulated that oxidative addition of the palladium catalyst to the diazonium intermediate is not the rate-determining step, in contrast to the generally accepted mechanism of aryl bromides and aryl chlorides.[1b] To go further in the mechanistic aspects with our catalytic system, we conducted an electrospray ionization mass spectrometry (ESI-MS) study to detect oxidative addition species directly under reaction conditions. Since ESI-MS is a soft ionization mass spectrometry,[6] its ability to detect ionic species in solution provides a convenient technique for direct observation of reaction intermediates.[7] ESI-MS has been applied to intermediate detection in several Heck reactions using aryl triflates and aryl iodides.[7c−e] An equimolar amount of arenediazonium tetrafluoroborate **2a** was added to Pd(0) complex **1** in methanol. Nitrogen was evolved immediately, and the mixture was injected to the mass spectrometer for analysis. Although our ESI-MS study does not provide quantitative or detailed structural information about the intermediates, we have been able to observe one peak at $m/z = 946$ corresponding to the [macrocycle-Pd$^+$ + Ar] ion with the predicted isotope pattern. After the addition of the olefin, samples of the reaction taken at 10 min intervals were injected for analysis until completion of the reaction. We did not observe any intermediate involving the olefin, but when the intermediate resulting from oxidative addition started to disappear, a peak corresponding to catalyst **1** ($m/z = 870$) emerged. Experiments were repeated for diazonium salts **2b**, **2f**, and **2g**, and we observed the corresponding oxidative addition species for all cases (**2b**, $m/z = 991$; **2f**, $m/z = 960$; **2g**, $m/z = 964$).

In conclusion, Pd(0) complex **1** is a recoverable phosphine-free catalyst with high activity for the Heck reaction of diazonium salts with acrylates and styrene to form the corresponding (*E*)-cinnamates and (*E*)-stilbenes respectively, affording excellent yields. ESI-MS studies provide mechanistic evidence for oxidative addition species formed in the catalytic cycle. Current studies are directed toward the characterization of the intermediates by NMR techniques.

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Supporting Information Available: Details of synthesis and characterization data for Pd(0) complex **1**, diazonium salts **2a**−**g**, and compounds **6a**−**g**, **7a**−**g**, and **8a**−**d**. Observed electrospray mass spectra and calculated isotopic distributions for ESI-MS studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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