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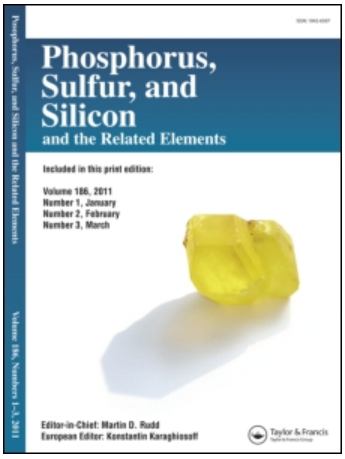

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
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Pd-Catalyzed Arylation of Phosphines: Reversibility and Ligand Exchange Issues

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To cite this Article Pietrusiewicz, K. Michał , Dziuba, Kamil and Kużnikowski, Maciej(1999) 'Pd-Catalyzed Arylation of Phosphines: Reversibility and Ligand Exchange Issues', Phosphorus, Sulfur, and Silicon and the Related Elements, 147: 1, 319
To link to this Article: DOI: 10.1080/10426509908053640
URL: http://dx.doi.org/10.1080/10426509908053640

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Phosphorus, Sulfur and Silicon, 1999, Vol. 147, pp. 319-319
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Pd-Catalyzed Arylation of Phosphines: Reversibility and Ligand Exchange Issues

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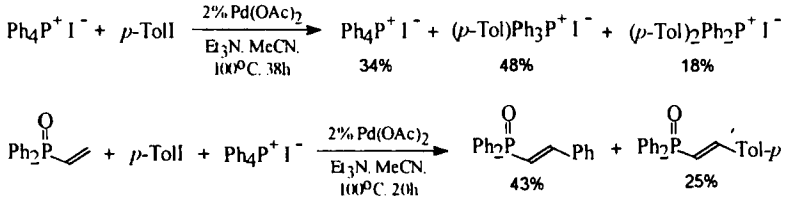
Our studies on the fate of the phosphine co-catalyst in the Heck arylation reaction have revealed that the quaternary tetraarylphosphonium cations which are formed from triphenylphosphine and aryl iodide under the reaction conditions undergo an aryl exchange process with the aid of the palladium catalyst. Independent exchange studies as well as model Heck arylation reactions carried out in the presence of stoichiometric amounts of tetraphenylphosphonium iodide demonstrated clearly that the Pd-catalyzed aryl exchange between aryl iodide and tetraarylphosphonium cation is a facile process which can effectively compete with the Heck arylation. The observed exchange process is reversible and involves triarylphosphines as discrete intermediates.



Pentaarylphosphoranes are not intermediates. The effects of the ring substituents in aryl iodides and tetraaryl phosphonium cations on the facility and extent of the exchange has been elucidated. Emerging synthetic applications of this novel Pd-catalyzed aryl exchange process have also been delineated.