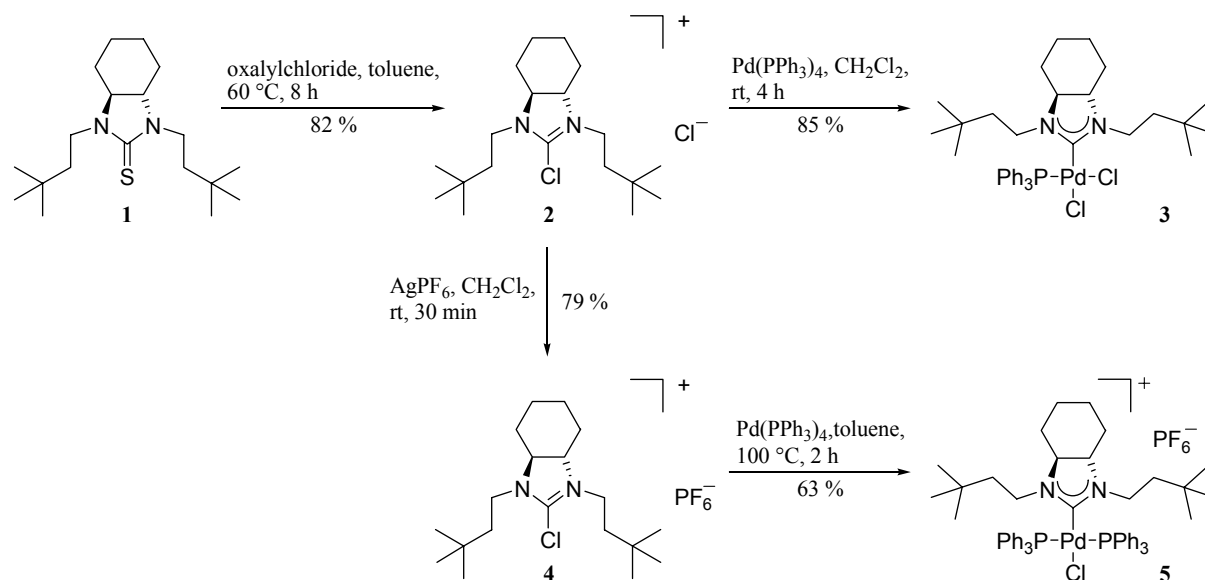


Research summary

Transition-metal complexes with *N*-heterocyclic carbene (NHC) ligands show considerable potential as catalysts for organic synthesis and fine chemical production.¹

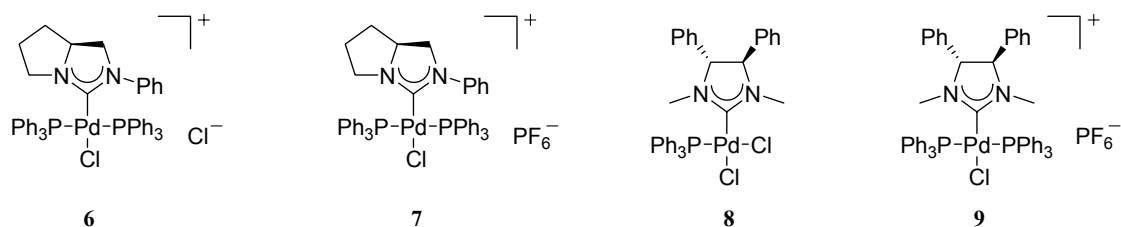
They are usually prepared *via* reaction of the appropriate carbene, formed as a discrete or a transient species, with a suitable metal precursor.² In none of these established procedures does the metal template change its oxidation state. Although these methods are widely applicable, the conditions used for the generation of the required *N,N'*-disubstituted imidazol(idin)-2-ylidenes are somewhat limiting, because they require either strongly basic or highly reducing media and/or involve thermal stress.

An alternative synthesis of (chiral) palladium complexes bearing NHC ligands involves the oxidative addition of Pd(PPh₃)₄ to easily accessible (enantiopure) 2-chloro-1,3-disubstituted imidazolium salts.³ The required 2-chloro-1,3-disubstituted imidazolium salts can be easily prepared from the corresponding thioureas or ureas. Both chloride and hexafluorophosphate salts may be used in this procedure (scheme 1).



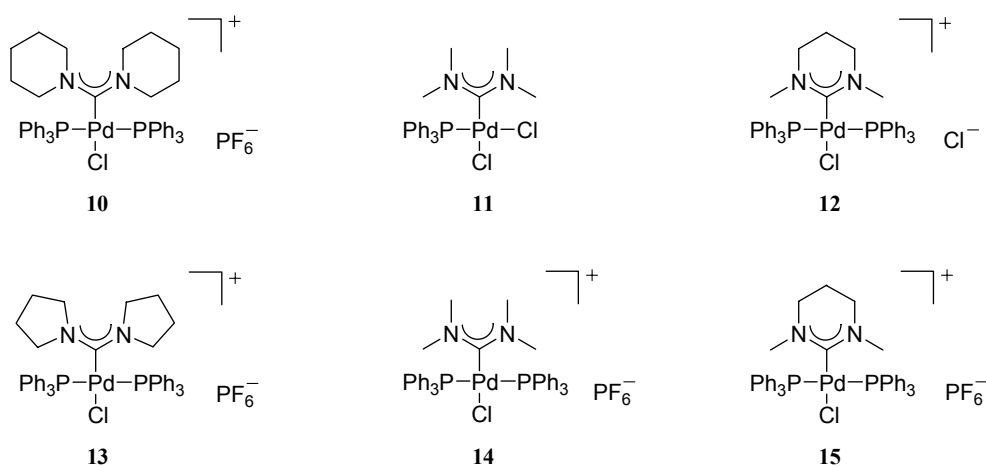
Scheme 1: Synthesis of NHC-Pd-complexes *via* oxidative addition.

In view of the host of 1,2-diamines that are commercially available in optically pure form, or are accessible by various well-established procedures, a wide variety of chiral Pd-complexes with NHC-ligands can be synthesized using this new protocol (scheme 2).



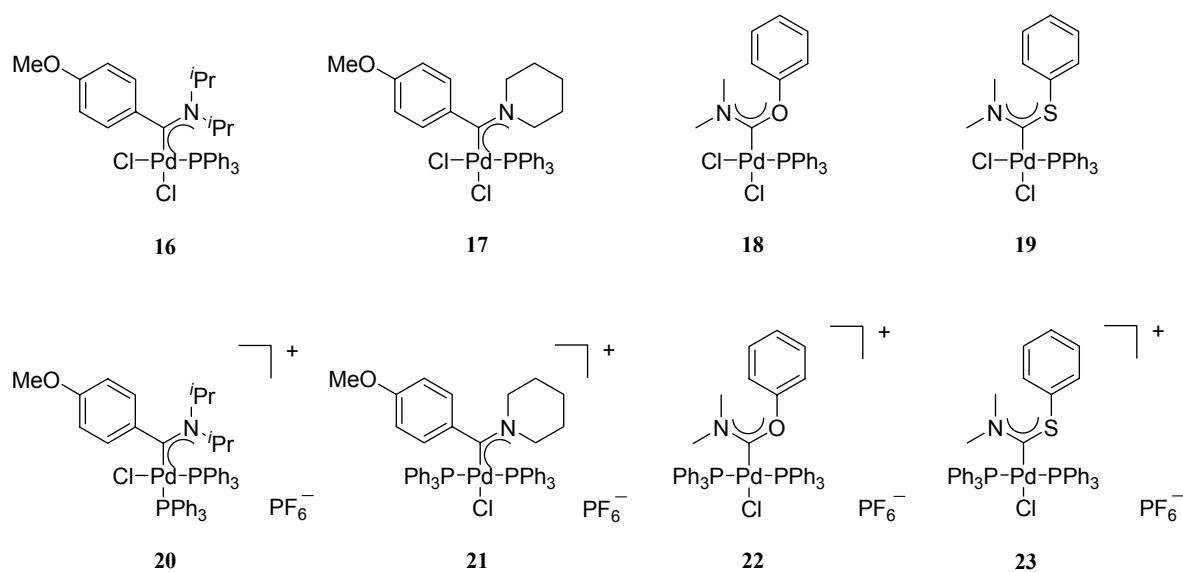
Scheme 2: Chiral NHC-Pd-complexes.

Furthermore it is possible to form Pd-NHC-complexes with interesting structures by this method. Both acyclic bis(dialkylamino)-carbene-Pd-complexes and 6-membered-NHC-Pd-complexes can be obtained (scheme 3). To the best of our knowledge, these are the first examples in the literature of these kind of Pd-NHC-complexes.



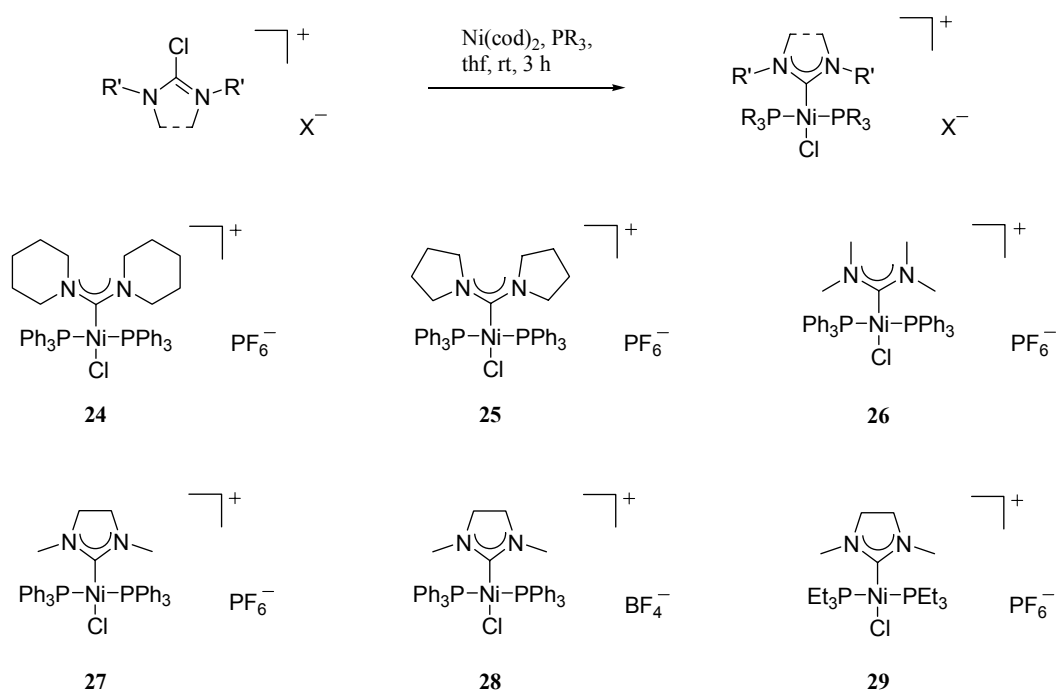
Scheme 3: New types of Pd-carbene-complexes.

In addition to that the developed method allows access to aminoaryl-, aminooxy- and aminothiocarbene-Pd-complexes (scheme 4).



Scheme 4: Synthesis of aminoaryl-, aminooxy- and aminothiocarbene-Pd-complexes *via* oxidative addition.

Moreover, it is possible to synthesize new Ni-carbene complexes *via* oxidative addition of Ni(cod)₂. Both cyclic and acyclic bis(dialkylamino)-carbene-Ni-complexes have thus been prepared (scheme 5).



Scheme 5: Synthesis of Ni-carbene-complexes *via* oxidative addition.

Preliminary experiments show that these novel carbene-complexes are active catalysts for C-C-coupling reactions (e.g. *Heck*-reaction, *Suzuki*-reaction, *Kumada*-reaction) and the *Hartwig-Buchwald*-reaction.

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