

SYNLETT Spotlight 441

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

2-(Pentafluorophenyl)imidazolidines

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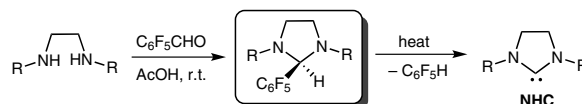
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Introduction

N-Heterocyclic carbenes (NHCs) have emerged as a unique class of organocatalysts and as ligands for transition metals.¹ The high reactivity of free NHCs, which makes these compounds very useful, translates into their sensitivity towards air and moisture. That is why NHCs are generally prepared in situ by deprotonation of azolium salts with strong non-nucleophilic bases [e.g., *t*-BuOK or KN(SiMe₃)₂]. The use of strong bases which are incompatible with many functional groups and the formation of typical byproducts (e.g., inorganic salts and alcohols) limit the scope of this method. An alternative approach to NHCs includes thermolysis of imidazolium-2-carboxylates, 2-(trichloromethyl)imidazolidines, silver–NHC complexes and other reagents. However, many of these reagents are poorly soluble. Moreover, they are commonly synthesized from NHCs. In 2004, Waymouth, Hedrick,

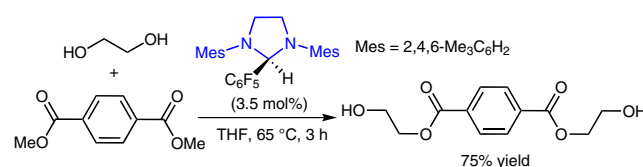
and co-workers reported the synthesis of 2-(pentafluorophenyl)imidazolidines as useful and readily available NHC-transfer reagents (Scheme 1).² The advantages of pentafluorophenyl adducts are: (a) high stability in air; (b) good solubility in common organic solvents; (c) thermolysis generally occurs under mild heating; (d) the only by-product of the thermolysis is pentafluorobenzene; (e) straightforward synthesis. 2-(Pentafluorophenyl)imidazolidines can be prepared from structurally diverse diamines and commercially available pentafluorobenzaldehyde (Scheme 1).



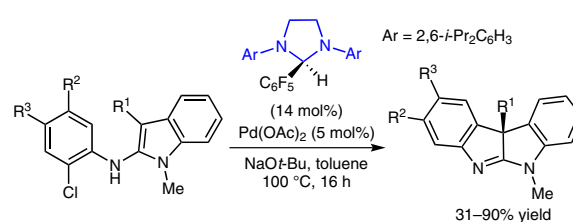
Scheme 1 Synthesis and thermolysis of 2-(pentafluorophenyl)imidazolidines^{2,3}

Abstracts

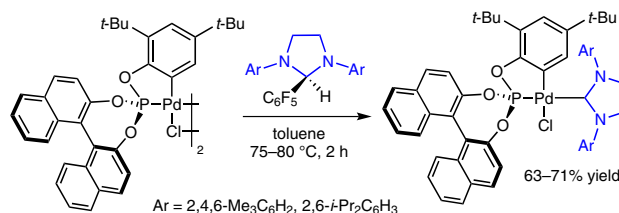
(A) Pentafluorophenyl adducts have been shown to be effective transesterification catalysts. Transesterification of dimethyl terephthalate with excess ethylene glycol to give bis(2-hydroxyethyl) terephthalate, an important precursor to poly(ethylene terephthalate), was investigated.²



(B) Previously unknown indoloindoles were prepared via a palladium-catalyzed dearomatization reaction.⁴ The catalyst used was formed in situ from palladium acetate and the pentafluorobenzene adduct of the carbene ligand.



(C) The preparation of chiral palladacycles from BINOL-based palladium complexes and pentafluorophenyl adducts was described.⁵ It was reported before that the reaction of free carbene, prepared from the respective imidazolium salt, with related palladium complexes did not proceed cleanly and gave a mixture of compounds.⁶ However, the same reaction with pentafluorophenyl adduct worked well to produce the desired product in 68% yield.



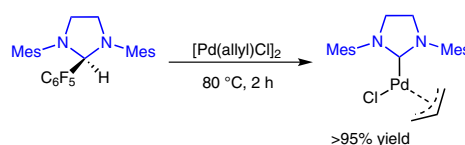
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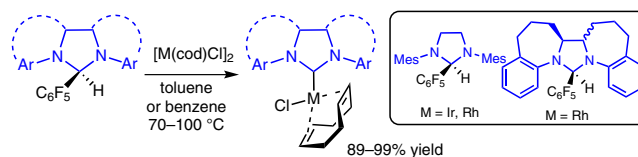
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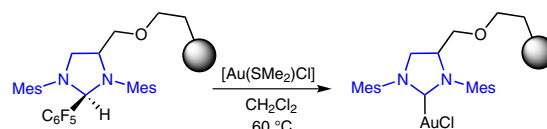
(D) Waymouth, Hedrick, and co-workers reported the synthesis of a palladium complex.² Treatment of $[\text{Pd}(\text{allyl})\text{Cl}]_2$ with pentafluorophenyl adduct at 80 °C in toluene gave the desired product in more than 95% yield. Moreover, the authors reported that this reaction can be carried out in air without prior solvent purification.



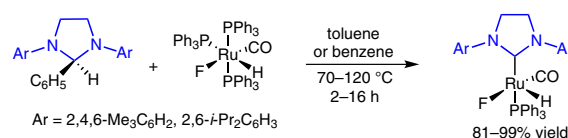
(E) Grubbs and co-workers used pentafluorophenyl adducts for the synthesis of iridium and rhodium complexes in excellent yield.^{3,7} Pentafluorophenyl adducts were chosen as carbene precursors rather than the traditional imidazolium salts in order to allow ligation onto metal fragments in the absence of a strong base.



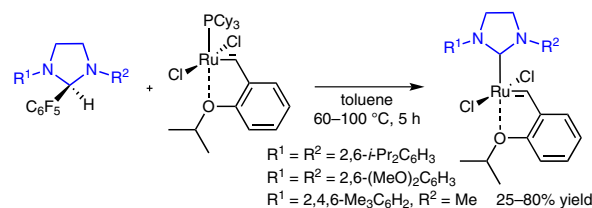
(F) Trapp and co-workers described the synthesis of gold and ruthenium catalysts using pentafluorophenyl adduct coated onto the inner surface of fused-silica capillaries.⁸ The authors have mentioned that the advantage of using pentafluorophenyl adduct is that the bonded carbene can be thermally generated and immediately converted into the bonded catalysts.



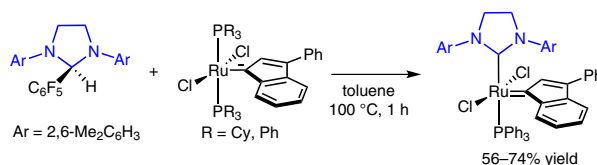
(G) The two new ruthenium complexes of the general formula $\text{Ru}(\text{NHC})(\text{PPh}_3)\text{F}(\text{CO})\text{H}$ and $\text{Ru}(\text{PPh}_3)_3\text{F}(\text{CO})\text{H}$ complex.⁹ The synthesized compounds were shown to be effective catalysts for hydrodefluorination of aromatic hydrocarbons.



(H) Grubbs–Hoveyda 2nd generation catalysts were prepared utilizing pentafluorophenyl adducts.³ The complex containing a methoxy groups was obtained in 25% yield. However, other methods that were attempted to prepare this complex were unsuccessful, highlighting the utility of pentafluorophenyl adducts.



(I) Verpoort and co-workers reported a straightforward synthesis of ruthenium–indenylidene-type complexes by a ligand-exchange reaction.¹⁰ The use of pentafluorophenyl adducts allowed to obtain the desired products in good yield without any chromatographic purification.



References

- (1) (a) Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612. (b) Grossmann, A.; Enders, D. *Angew. Chem. Int. Ed.* **2011**, *51*, 314.
- (2) Nyce, G. W.; Csihony, S.; Waymouth, R. M.; Hedrick, J. L. *Chem.–Eur. J.* **2004**, *10*, 4073.
- (3) Blum, A. P.; Ritter, T.; Grubbs, R. H. *Organometallics* **2007**, *26*, 2122.
- (4) Bedford, R. B.; Fey, N.; Haddow, M. F.; Sankey, R. F. *Chem. Commun.* **2011**, *47*, 3649.
- (5) Bedford, R. B.; Dumycz, H.; Haddow, M. F.; Pilarski, L. T.; Orpen, A. G.; Pringle, P. G.; Wingad, R. L. *Dalton Trans.* **2009**, 7796.
- (6) Bedford, R. B.; Betham, M.; Blake, M. E.; Frost, R. M.; Horton, P. N.; Hursthouse, M. B.; López-Nicolás, R.-M. *Dalton Trans.* **2005**, 2774.
- (7) Li, J.; Stewart, I. C.; Grubbs, R. H. *Organometallics* **2010**, *29*, 3765.
- (8) Lang, C.; Gärtner, U.; Trapp, O. *Chem. Commun.* **2011**, *47*, 391.
- (9) Reade, S. P.; Mahon, M. F.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2009**, *131*, 1847.
- (10) Monsaert, S.; Canck, E. D.; Drozdak, R.; Van Der Voort, P.; Verpoort, F.; Martins, J. C.; Hendrickx, P. M. S. *Eur. J. Org. Chem.* **2009**, 655.