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Electrocatalytic Assistance by Nickel Complexes of a Coupling Reaction between Alkenes and Aromatic Halides leading to Substituted Olefins

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Electrochemical generation of organonickel–phosphine complexes affords a new catalytic route to substituted olefins *via* the coupling of aromatic halides and alkenes.

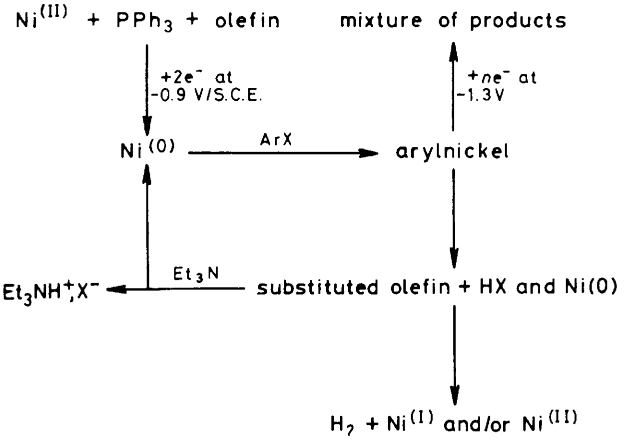
Substituted olefin monomers are of great interest in the production of homo- and co-polymers. Catalytic preparations of such compounds from aromatic halides (ArX) and olefins have been described, principally using organopalladium compounds.[1] When nickel catalysts are used, the process requires harsh conditions and is not very selective.[2]

We present here a new catalytic route *via* an electrochemical method for the formation of substituted olefins under mild conditions, according to the general reaction shown in equation (1). This reaction was catalysed by nickel complexes

$$\mathrm{ArX} + \mathrm{RCH{=}CH_2} \xrightarrow{\mathrm{Ni}} \mathrm{RCH{=}HCAr} + \mathrm{HX} \qquad (1)$$

which were electrochemically generated and maintained *in situ*.[3] The solvent was *N*-methyl-2-pyrrolidone (NMP) or a mixture of tetrahydrofuran (THF) and hexamethylphosphoramide (HMPA); $LiClO_4$, NBu_4I, or KI were used as supporting electrolytes, and the temperature was maintained between 25 and 50 °C. Ni^{II} was electroreducible in two steps, the potentials of which depended on the ratio of ligand to Ni^{II}, and the nature of the associated anion [-0.75 and -0.9 V *cf.* standard calomel electrode (S.C.E.) if $NiI_2(PPh_3)_2$ was used with KI as the electrolyte in the presence of an olefin, *e.g.* C_2H_4 at atmospheric pressure]. Electrolysis of the nickel-containing solution on a gold gauze at the potential of the second reduction step produced a stable yellow electro-oxidizable, zerovalent nickel complex, probably associated with the phosphine and olefin.

When ArX was added, the oxidative addition of Ni^0 to ArX was observed, the kinetics of which could be followed by amperometry at the potential of the oxidation step of Ni^0.[3c] A σ-arylnickel complex was obtained, which was stable enough to be detected (reduction at -1.3 V), however it decomposed after a few minutes to give the substituted olefin. In such cases a maximum of 2 substituted olefins per Ni atom were obtained and Ni^{II} was recovered. The system continued to function while electricity was consumed, enabling the Ni^0 catalyst to be regenerated. If a base, like Et_3N, was added simultaneously with ArX, the reaction was faster and the amount of substituted olefin exceeded twice the initial amount of nickel. However, even in this case, it was necessary to maintain the catalytic system, by electroreduction, since deactivation gradually occurred by regeneration of Ni^{II}. When a mixture of THF–HMPA was used as the solvent, the electrocatalytic synthesis could be performed in a 'one pot' reaction using NiX_2, PPh_3, ArX, olefin, and a large excess of Et_3N. This was not possible in the solvent



Scheme 1

Table 1

ArX[a]	Olefin (1 atm)	Product and yield/%[b]	
PhI (10/9)	C_2H_4	Styrene	80
PhI (20/18)	C_2H_4	Styrene	65
PhBr (10/8)	C_2H_4	Styrene	70
PhCl (10/7)	C_2H_4	Styrene	50
p-IC_6H_4OH (10/9)	C_2H_4	*p*-HO-styrene	70
p-BrC_6H_4OMe (10/9)	C_2H_4	*p*-MeO-styrene	70
PhI (10/2)	C_3H_6	α- and β-Methylstyrene	55
PhBr (10/8)	C_3H_6	α- and β-Methylstyrene	65
PhI (5/3)	$PhCH=CH_2$[c]	*trans*-Stilbene	50

[a] Values in parentheses are the initial and converted amounts, respectively, in mmol. [b] Yields are with respect to converted ArX. [c] 10 mmol.

NMP where the amine strongly complexed the Ni^{II} salts. We assumed that the hydrogen which was displaced from the olefin by substitution with the aromatic group, reacted either in a redox reaction regenerating Ni^I and/or Ni^{II} or concurrently in a acid–base reaction when amine was present. Scheme 1 summarises the different steps which may be involved.

When the olefin was ethylene and ArX a halobenzene the main product was styrene. Other products such as benzene, ethylbenzene, and biphenyl were also obtained in small amounts (about 5 to 10% of PhX converted). The chemical yield of conversion of PhX into styrene was high (90 to 95%). However although the concentration of styrene may have increased, the yield may fall since some styrene is converted into stilbene or polymerised. Electrolyses were carried out in a two-compartment cell (30 ml each). The amount of catalyst precursor used was 1 mmol, ArX and Et_3N were added in the range of 5 to 20 mmol, and the potential was maintained at the value of the formation of Ni^0. Electrolyses were stopped when the current intensity was less than 5 mA (initial current was about 150 mA). Identification and yields of products were determined by mass spectroscopy and g.l.c. See Table 1 for results.

Since the arylnickel complex was reducible at −1.3 V, electrolysis could also be carried out at this potential. The conversion of ArX occurred faster at this potential, but the side products, especially ArH and Ar–Ar were obtained in larger proportions (30 to 50%). We assumed that electroreduction of ArNiX afforded very active anionic species leading to biaryls and arenes as we have already reported in earlier work.[4] In this connection we would like to point out that more side reactions may occur from the reduction of arylnickel complexes when a chemical reducing agent such as Zn is used.[2] This emphasises the significance of the electrochemical process which allows a better selectivity by controlling the potential of reduction, thereby limiting or avoiding side reactions.

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