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PREPARATION AND SYNTHETIC USE OF THE ZEROVALENT NICKEL COMPLEX BY ELECTROCHEMICAL REDUCTION

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Summary: The generation of $Ni(PPh_3)_4$ by electrochemical reduction was carried out in a divided cell containing $NiCl_2(PPh_3)_4$, PPh_3 and $n\text{-}Bu_4NBr$ in DMF with a lead plate as cathode and a platinum plate as anode under the stream of argon at 60°. Using this $Ni(PPh_3)_4$, biphenyls and the heterocyclic compounds were synthesized in fairly good yields.

Synthetic utility of the zerovalent nickel complex is now generally recognized, which involves, for example, the synthesis of biphenyls,[1] the generation of π-allylnickel compounds,[2] and the synthesis of arylnickel or vinylnickel complex.[3] We have already reported the synthesis of heterocyclic compounds via arylnickel complexes,[4] for which the zerovalent nickel complex[$Ni(PPh_3)_4$] was prepared by the known methods,[5] but the simplification of those methods was desired. In order that the divalent nickel complex should be reduced to the zerovalent nickel complex, the electrochemical process might be considered.

$$Ni^{II} \xrightarrow{e^-} Ni^{I} \xrightarrow{e^-} Ni^{0}$$

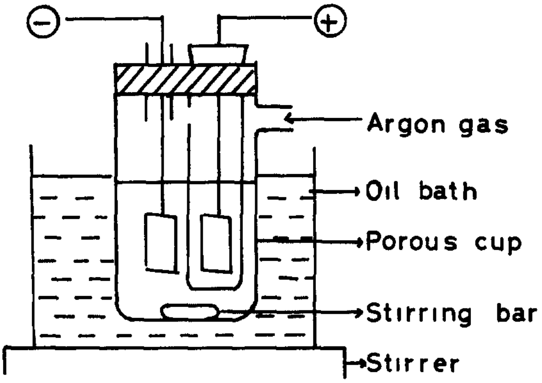
Although several methods[6] have been already reported due to this idea, they are not suitable for our synthetic purpose. Now we report the new electrochemical method of preparation of $Ni(PPh_3)_n$, and the synthesis of biphenyls and the heterocyclic compounds using this zerovalent nickel complex.
A typical procedure is shown in the following.

A mixture of $NiCl_2(PPh_3)_2$(326.5 mg, 0.5 mmol), PPh_3(262 mg, 1.0 mmol) in DMF (8 ml) containing $n\text{-}Bu_4NBr$(0.1 M solution) as supporting electrolyte in a divided cell was electrolyzed with a lead plate as cathode and a platinum plate as anode as shown in Figure 1. During the current was passed under the stream of argon at 60°, the color varied from initially blue to red. After 2F/mol had been passed, the electrodes were withdrawn and then p-bromotoluene(85.5 mg, 0.5 mmol) in DMF(3ml) was added under the stream of argon. The whole mixture was warmed at 65° under an atmosphere of argon for 20 h to give 4,4'-dimethylbiphenyl[33.9 mg, 74.5%, mp 110-111°(lit. 112°)[1b]].
The same treatment of various halobenzenes gave the corresponding biphenyls in addition to a small amount of phosphine derivatives(3) as shown in Table 1. The latter compound(3) must be obtained from the phosphonium salt(5) through the

Scheme 1.[7] These results suggest that $Ni(PPh_3)_n$ generated by electrochemical reduction is effective for the synthesis of biphenyls.

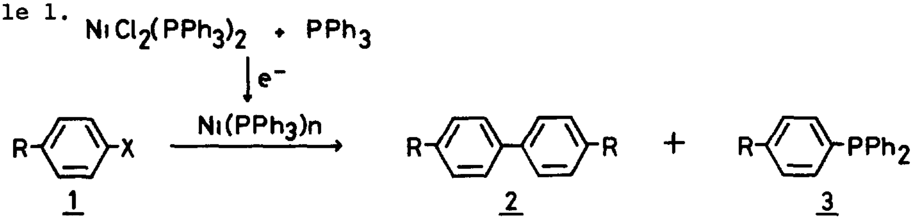
On the other hand, the synthesis of oxindole derivatives from o-chloroaniline derivatives using $Ni(PPh_3)_n$ was already reported by us,[4a,b] in which the zero-valent nickel complex was prepared from $Ni(acac)_2$ and $AlEt_3$, or $NiCl_2(PPh_3)_2$ and Zn in the presence of PPh_3.

Figure 1



Cathode;	Pb
Anode;	Pt
Electrolyte;	$n-Bu_4N$
Solvent;	DMF

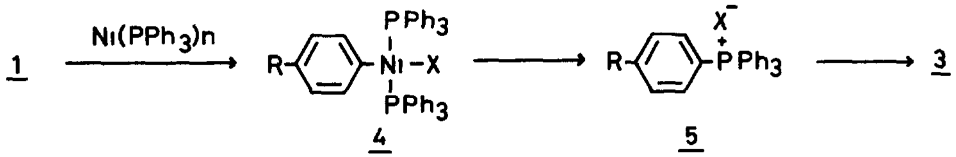
Table 1.



	1		Time(h)	Yields(%) of		
	R	X		2*	3	1
a	H	Br	4	79.9		
b	COMe	Br	14.5	46.9	13.2	3.3
c	COOMe	Cl	21.5	51.1	4.3	14.0
d	Me	Br	20	74.5		
e	OMe	Br	17	35.9		15.4

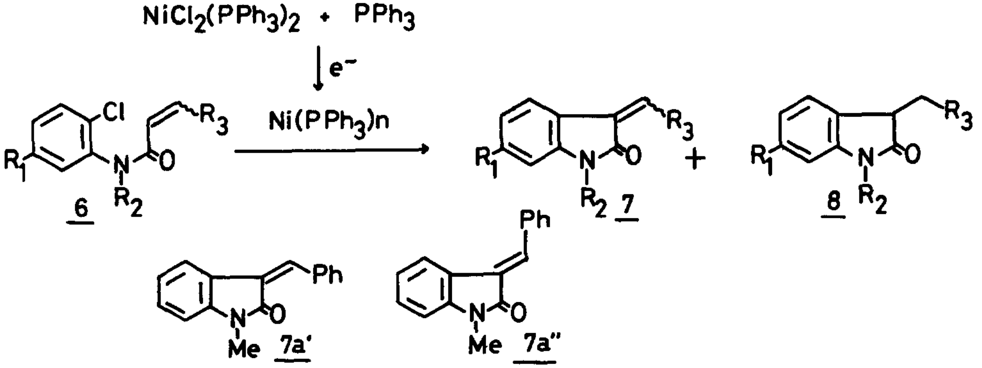
* The melting point of each biphenyl agreed with those of the literature.[1b]

Scheme 1.



synthesis of these oxindole derivatives using Ni$(PPh_3)_n$ by previous electrochemical reduction was tried, on which the compound(6a) was added to the DMF solution containing Ni$(PPh_3)_n$ generated by electrochemical reduction of $NiCl_2(PPh_3)_2$ in the presence of PPh_3 in the same manner as the synthesis of biphenyls. The whole mixture was warmed at 70° for 4 h to give the expected oxindole derivatives(7a', 45.4%, 7a", 9.8%, 8a, 7.6%, respectively) in addition to the starting material(6, 27.7%). These results are summarized in Table 2.

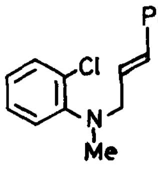
Table 2.



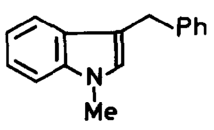
	6			Yields(%) of		
	R_1	R_2	R_3	7	8	6
a	H	Me	Ph	54.8(65.9)*	7.6	27.7
b	OMe	CH_2Ph	CN(Z-isomer)	22.6(4.8)	39.9(39.1)	
c	OMe	CH_2Ph	CN(E-isomer)	12.0(20.4)	53.3(45.5)	
d	H	CH_2Ph	COOMe		40.2	26.8

* The yields of oxindole derivatives using Ni$(PPh_3)_4$ prepared by chemical method were shown in parentheses.[4a,b]

Subsequently, a solution containing $NiCl_2(PPh_3)_2$, PPh_3, n-Bu_4NBr and the compound(9) or (11) were electrolyzed under a controlled potential of -1.9V, in which a platinum wire was used as a reference electrode.[6a] After 2F/mol was passed, an expected indole(10, 35.1%) or benzazepinone derivative(12, 13.9%) was obtained.



9



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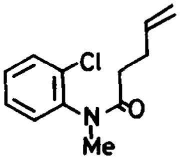

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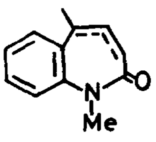
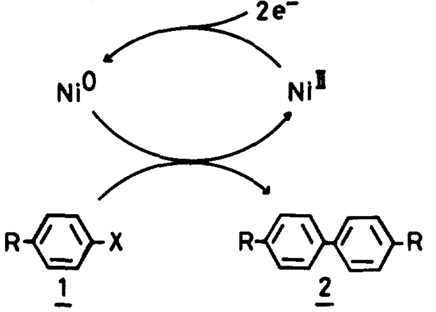
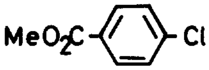
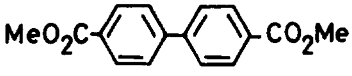


12

In line with this idea, the current was passed at 65° under a controlled potential of -1.9V to a DMF solution containing $NiCl_2(PPh_3)_2$(0.1 mmol), PPh_3 (0.2 mmol), methyl p-chlorobenzoate(1c, 0.5 mmol) and n-Bu_4NBr(0.1 M solution). After 2.0 F/mol was passed, 4,4'-dicarbomethoxybiphenyl(2c) was obtained in the yield of 44.4%.




1c


2c

The preparation of $Ni(PPh_3)_n$ by electrochemical reduction has been turned out to be a very useful synthetic tool since handling is very easy and a reducing reagent is not present in the reaction medium.

Further studies are in progress.

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