

Anodically Induced Decomposition of some Arylnickel(II) Phosphine Complexes

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Summary Anodic oxidation of complexes $[(PEt_3)_2Ni(Ar)R]$, coupling products $Ar-R$ and/or to formation of radicals.
Ar = aryl, R = aryl or methyl, leads to formation of the _____

It is believed that complexes of the type $[L_2Ni(R^2)R']$ are formed during the nickel-catalysed cross coupling of alkyl and aryl halides with organometallic reagents, and it has recently been suggested that the coupling product is formed by reductive elimination from an ion of the type $[(PEt_3)_2Ni(R')R]^+$ (1).¹ In order to test this suggestion we have studied the anodic oxidation of the complexes $[(PEt_3)_2Ni(o\text{-tolyl)Me}]$ (2), $[(PEt_3)_2Ni(\text{mesityl})_2]$ (3), and $[(PEt_3)_2Ni(o\text{-tolyl})_2]$ (4) with cyclic and single sweep voltammetry and with constant current electrolysis. The results are summarised in the Table.

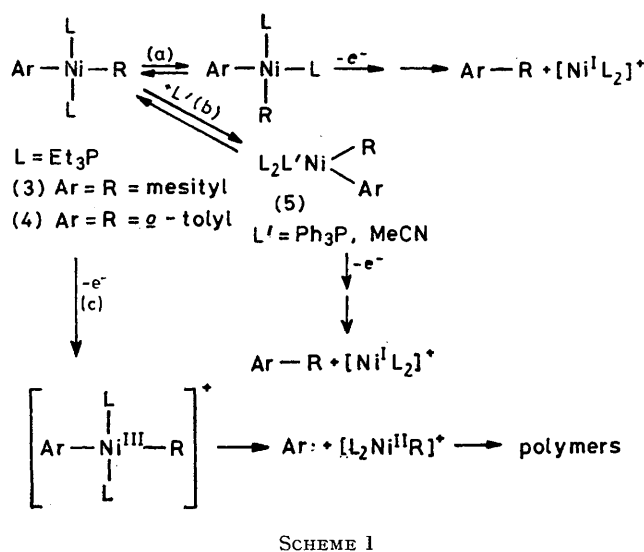
TABLE

Complex	E (anodic)/V ^a	F/mol consumed on electrolysis ^b	% Yield of coupling product ^c
(2)	ca. 0.55 ^d	(1.2)	— ^e
(3)	0.58	24.0	ca. 1
(4)	0.67 ^f	1.6	68 ^{g,h}
(4) + PPh ₃	0.54; 0.68	—	—
(4) in MeCN	0.47	1.5	94

^a Ionic medium 0.1 M Bu₄NBF₄ in CH₂Cl₂ (MeCN when noted), reference electrode Ag, AgCl/0.1 M LiCl(aq.), Pt button working electrode, sweep rate 100 mV s⁻¹, temperature 23 ± 2 °C. ^b Electrolysis continued until the potential of the anode rose above E_p (anodic) and no complex could be detected by voltammetry. ^c The coupling products were identified using g.l.c. Yields were also determined by g.l.c. (2) gave *o*-xylene, (3) gave bimesityl, and (4) gave *o*-bitolyl. ^d The peak was very broad and ill-defined. ^e The yield of *o*-xylene from the electrolytic reaction could not be determined owing to extensive parallel thermal formation. ^f A small pre-peak, ca. 1/6 of the height of the main peak, was observed at ca. 0.45 V. ^g Control experiments showed that a 19% yield of *o*-bitolyl was formed thermally from (4) in CH₂Cl₂ and a 28% yield from (4) in MeCN during the time required for the electrolysis. ^h The yield was slightly increased on electrolysis at -50 °C.

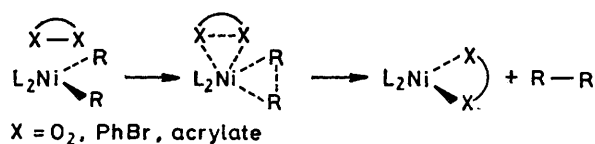
The complexes undergo one-electron oxidation, followed by a fast irreversible chemical reaction. The oxidised species from (3) was stable enough to be observed as a reduction peak at room temperature. The oxidised species from (4) could be observed at -50 °C. Exhaustive constant current electrolysis, carried out at a working electrode potential between E_p and $E_p + 0.2$ V, led to the formation of the following coupling products: from (2), *o*-xylene was obtained, from (3), bimesityl, and from (4), *o*-bitolyl were obtained (see Table). In addition, polymeric material was formed during the electrolyses, and only in the case of (4) in acetonitrile did the formation of the coupling product become nearly quantitative. The high yield of *o*-bitolyl indicates a concerted reductive elimination. It is possible that a five-co-ordinate species [Scheme 1, path (b)] is formed. The observed peak potential of (4) in acetonitrile (0.47 V) is rather close to the potential of the new peak (0.54 V), which appears if triphenylphosphine is added to a methylene chloride solution of (4) and which we ascribe to a five-co-ordinate complex with triphenylphosphine as the fifth ligand.

In methylene chloride solution both concerted and radical pathways appear to be open. Tsutsumi *et al.*² have shown that electrolytic oxidation of benzoic acid, which gives phenyl radicals, in the presence of aromatic hydrocarbons yields, among other products, polymers and phenylated hydrocarbons. Formation of polymeric material at the anode was also observed in the anodic oxidation of mesitylene



in methylene chloride.³ One of the major products of this oxidation was bimesityl, which was believed to be formed *via* mesitylene cation radicals. Formation of mesityl radicals by proton loss from the cation radicals would be a possible side reaction. It was noted that the formation of the polymer led to an increase of the current. Anodic oxidation of benzene in acetonitrile has also been reported to give oxidisable polymeric products, probably *via* phenyl radicals.⁴ It is therefore tempting to suggest that the polymeric material observed in this work and the high current consumption in the electrolysis of (3) are caused by the formation of radicals according to Scheme 1, path (c). Theoretical studies indicate that a *cis* arrangement of the aryl (or alkyl) groups is required for concerted reductive elimination.⁵ It is therefore reasonable to assume that decomposition takes place *via* both concerted [path (a), Scheme 1] and radical [path (c), Scheme 1] pathways. It is particularly instructive that the dimesityl complex (3) gives almost exclusively polymeric material in a reaction which requires ca. 20 F mol⁻¹. Owing to the bulk of the mesityl groups, they should not readily attain a *cis* configuration. Path (c) would thus be strongly favoured, as indicated by the experimental evidence.

Special conditions are apparently necessary, if nickel(III) diaryls and similar compounds are to undergo efficient reductive coupling. This may also explain why Chen and Kochi did not report any formation of bialkyls in their recent study of electrolytic (and chemical) oxidation of dialkylplatinum(II) species.⁶ The promotion of reductive coupling by bromobenzene and oxygen¹ could therefore have another origin than simple one-electron transfer from nickel(II). Yamamoto *et al.*⁷ have shown that acceptor olefins



SCHEME 2

promote reductive elimination. A mechanism involving concerted cycloaddition-elimination, Scheme 2, appears attractive for this reaction and could also explain the effect of oxygen and bromobenzene.

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