Reductive versus coupling pathways in the reactions of nickel and copper vapours with the mono-halobenzenes

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Summary
The reactions of nickel and copper vapours with mono-halobenzenes to form benzene and biphenyl are reported. Benzene formation apparently proceeds through the intermediacy of the phenyl radical, which is produced when metal clusters abstract halogen from the halobenzene. Biphenyl formation proceeds via an oxidative insertion/disproportionation/reductive elimination sequence, and requires that metal atoms, rather than metal clusters, initiate the reaction sequence. The concentration of the metal in the matrix determines the pathway of the reaction. Cluster formation and benzene production are favoured by high metal concentrations, while low metal concentrations in the matrix favour biphenyl production. Copper vapours are anomalously less reactive than nickel vapours, even though copper reagents are used in the Ullmann reaction to produce biaryls through the coupling of haloarenes. This result appears to be due to the preferential formation of atoms or very small clusters over large clusters or crystallites under the conditions of the metal vapour synthesis technique.

Introduction
The heterogeneous Ullmann reaction\(^{(1)}\) is a widely used method for the coupling of haloarenes to produce many symmetrical and unsymmetrical biaryls through the use of copper powder as a reagent\(^{(2)}\). Relatively high temperatures are required for the traditional Ullmann reaction (up to 300 °C in refluxing solvent\(^{(3)}\)). However, milder conditions (as low as 0 °C) are possible with a copper reagent prepared by the reduction of copper(I) salts with lithium or potassium naphthalenide\(^{(4,5)}\).

The mechanism for the heterogeneous Ullmann reaction is thought to be that depicted in Figure 1(a)\(^{(5-6)}\). There are apparently no free radical intermediates involved in the process\(^{(5-6)}\). The Ullmann reaction can also be carried out under homogeneous conditions using soluble copper(I) salts; the mechanism of the homogeneous reaction is similar (Figure 1(b))\(^{8,10}\).

The coupling of haloarenes to biaryls can also be accomplished using activated nickel powders\(^{(11,12)}\) or soluble nickel complexes\(^{(12,13)}\). The mechanism of the heterogeneous reaction\(^{(11,12)}\) is thought to be that depicted in Figure 2a, where a classical oxidative addition/disproportionation/reductive elimination sequence occurs. In the homogeneous reactions, however, detailed studies led to two alternative mechanisms, each with significant differences from what is thought to occur in the heterogeneous reaction.

Beginning with isolated and characterized arylnickel(II) halide complexes of phosphines, Tsou and Kochi\(^{(12)}\) concluded that phosphine complexes of nickel(I) and arylnickel(III) halides were reactive intermediates in a radical chain process which produced biaryls from haloarenes (Figure 2b). Free radicals were conclusively eliminated as possible intermediates in their reaction system. Conversely, in the work of Semmelhack and co-workers\(^{(13)}\), a second oxidative insertion (following an oxidative insertion on the nickel(0) starting material to form a nickel(II) intermediate) to form a nickel(IV) intermediate is proposed. This nickel(IV) species then reductively eliminates the biaryl (Figure 2c).

The technique of Metal Vapour Synthesis (MVS)\(^{(14,15)}\) can provide a method for the preparation of activated metal powders or slurries (aluminium, indium, zinc, cadmium, tin, lead, and nickel). These slurries are useful in a variety of reactions with haloalkanes and haloarenes\(^{(14)}\). In some cases, aryl- and alkyl-complexes of metals may be isolated from these reactions. Unfortunately, reactions of haloarenes with nickel slurries do not result in high yields of biaryls.

In contrast with the apparently low reactivity of the nickel slurries produced by MVS toward haloarenes, certain haloarenes do react readily with nickel vapours after co-condensation at −196 °C to yield both the insertion product ArNi\(^{11}\)X and the disproportionation product ArNi\(^{11}\)Ar. When the haloarene is chloro-, bromo- or iodo-pentafluorobenzene, both of these

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Figure 2. Proposed mechanisms for the coupling of haloarenes using (a) heterogeneous nickel(0) reagents, (b) soluble, pre-formed arylnickel(II) halide complexes, and (c) soluble, nickel(0) complexes of cyclooctadiene or phosphines. In (a), \( L \) = solvent (the exact nature and number of associated solvent molecules are unknown), while in (b), \( L \) = phosphine ligand, and in (c), \( L_2 \) = cyclooctadiene or two phosphine ligands. Except for the explicitly isolated and characterized complexes in (b) and (c) \( i.e., \text{ArNi}^{I}_{L_2}, \text{Ni}^{I}_L \), respectively, the numbers of ligands have been arbitrarily assigned assuming four-coordinate complexes.

Intermediate can be trapped as the phosphine adducts, and the latter disproportionation product can be isolated as the \( \eta^2 \)-toluene adduct\(^{117} \).

The focal point of the reactions of metal vapours with haloarenes has always been the production of isolable metal complexes of the haloarenes. When no such complexes could be isolated, the organic products of the reactions, if any existed, were ignored\(^{18} \). We have begun a systematic investigation of MVS reactions with haloarenes which focusses specifically on the organic products of the reactions. In so doing, we hope to better delineate the intrinsic reactivity of the metal vapours with haloarenes and to study the reaction mechanisms involved when metal vapours interact with haloarenes. Further, we shall compare our results with those for the classical Ullmann reaction so as to determine how metal vapours are similar to or different than classical methods for the coupling of haloarenes. Herein we report our results for nickel and copper vapour reactions with the mono-halobenzenes.

**Experimental**

*Metal vapour co-condensation/addition (CCA) reactions*

A schematic diagram of the metal vapour co-condensation/addition (CCA) reactor is found in Figure 3. The metal (nickel, 99.9%, copper, 99.999%, Cerac, Inc.) to be vaporized is placed in an integral alumina-coated tungsten crucible (GTE Sylvania Emissive Products) connected to water-cooled copper electrodes. The reactor is evacuated under dynamic vacuum to approximately \( 1 \times 10^{-4} \) torr, and the external wall of the reactor bottom is cooled to \(-196 \) \(^\circ\)C with liquid nitrogen. At this point, previously degassed (by repeated freeze/pump/thaw cycles), dry, benzene-free toluene (Fisher ACS-certified) is inlet as a vapour through the shower-head, and the