

Preliminary communication

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THE ELECTROCHEMICAL PREPARATION OF ORGANO NICKEL AND PALLADIUM  
HALIDES

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Summary

The electrochemical oxidation of a nickel or palladium anode in the presence of certain organic halides yields the unstable RMX species, which can be stabilised by both mono and bidentate phosphorus(III) ligands. Cyanide compounds of the general formula  $RN_1CN.L_2$  can also be synthesised. The advantages of the method are outlined.

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The organohalide complexes of nickel, palladium and platinum have been the subject of a considerable amount of preparative and spectroscopic study. Since we are concerned here with a new preparative route, it is worth noting that the compounds  $RMXL_2$  have most often been prepared either by the reaction of the appropriate lithium aryl or alkyl with the metal dihalide, or via a Grignard reaction<sup>1</sup>. More recently, Klabunde and his co-workers<sup>2</sup>, and others<sup>3</sup>, have shown that the condensation of a metal vapour with the appropriate organic halide gives rise to the reaction



for nickel, palladium and platinum. Following established procedures<sup>1</sup>, the organohalides obtained in this way can be

stabilized by the addition of an organophosphine to give the four-coordinate  $RMXL_2$  complexes. Compounds derived from perfluoroalkyl or aryl halides have been of particular interest, and the stability of such compounds has been discussed in terms of both thermodynamic and kinetic factors<sup>1,4</sup>.

We have now shown that nickel and palladium compounds listed in the Table can be prepared from the metal by a direct electrochemical synthesis carried out at room temperature. This method has already been successfully used for the analogous compounds of cadmium<sup>5</sup> and tin<sup>6</sup>, and for alkyl and aryl halides of titanium, zirconium and hafnium<sup>7</sup>. In a typical experiment, a piece of nickel wire hammered into a rectangular sheet (area 1.5 cm<sup>2</sup>, thickness 0.5 mm) forms the anode of a cell in which the solution phase is 1:1 ethanol and pentafluorobromobenzene

Table. Organohalides of nickel and palladium prepared by direct electrochemical synthesis (a)

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$C_6F_5NiBr$	$C_6F_5PdBr.2Et_3P$
$C_6F_5NiBr.2Et_3P$	$C_6F_5PdBr.diphos$
	$C_6F_5PdBr.2py$ (unstable)
$CH_3NiCN.2CH_3CN$	
$CH_3NiCN.2Et_3P$	
$C_2H_5NiCN.2Et_3P$	
$C_6F_5NiCN.2Et_3P$	
$C_6H_5NiCN.2Et_3P$	
$C_6H_5CH_2NiCN.Et_3P$	
$C_6H_5CH_2NiCl$ (unstable)	

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(a) Metal and halogen analyses, and infrared spectra, established the formula in each case.

(total vol.  $2.2 \text{ cm}^3$ ) containing 20 mg of tetraethylammonium bromide; all solvents must be thoroughly dried. The cathode is a tungsten wire (2 cm long, 0.5 mm diam.) fused into the wall of the cell (dimensions approx. 14 cm long, 1.5 cm diam.). An applied potential of 20 V produces an initial current of 15 mA. After 12 hr of electrolysis, during which 107 mg of nickel dissolved, the solution was filtered to remove some decomposition products. The volume of the solution was reduced by half, and  $5 \text{ cm}^3$  of benzene added to remove the tetraethylammonium bromide, which was filtered off; on complete removal of solvent from the filtrate, yellow crystals formed, shown by analysis to be pentafluorophenylnickelbromide (yield 71.3%, based on nickel dissolved). This compound is extremely hygroscopic, but can readily be stabilized by the addition of triethylphosphine which produces yellow crystals of the adduct  $\text{C}_6\text{F}_5\text{NiBr}\cdot 2\text{Et}_3\text{P}$ . Similar procedures lead to the corresponding palladium compound. All experiments were carried out in an atmosphere of dry nitrogen.

We have also been successful in preparing a series of organo-nickel cyanides by similar methods, using a solution phase of RCN and methanol. These compounds, which are listed in the Table, and which are in some cases reported for the first time, are particularly interesting in view of the arguments advanced as to the stability of  $\sigma$ -bonded organo metal compounds, given the position of the cyanide ion in spectrochemical series.

The main advantages of this electrochemical method of preparation are those which have been stated earlier for this method<sup>4,5</sup>, namely that significant quantities of the compounds can be prepared at room temperature by the use of simple apparatus. We should mention finally one striking failure of the method; we have not been able to prepare any of the well-known  $\text{RPtXL}_2$  platinum complexes by these electrochemical methods. Work on this and other topics is proceeding.

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