# Preliminary communication

# Fluorophosphine-induced ligand coupling reactions of $\pi$ -allylnickel and -palladium complexes

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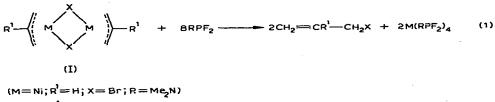
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 $\pi$ -Allylic acetylacetonatopalladium complexes readily afford allylic acetylacetones and palladium metal when treated with carbon monoxide at ordinary temperatures and pressures<sup>1, 2</sup>. Ligand coupling reactions have also been observed in  $\pi$ -allylpalladium compounds containing acetate<sup>3</sup>, amine<sup>3</sup> and allylic groups<sup>4</sup>, likewise bis( $\pi$ -allyl)nickel and carbon monoxide yield biallyl and nickel tetracarbonyl<sup>4</sup>.

In view of the known similarity in coordinating ability of fluorophosphines and carbon monoxide towards transition metals<sup>5</sup> and current interest<sup>6-10</sup> in the mechanism of the carbonylation of allyl halides catalysed by  $\pi$ -allylpalladium complexes we have studied the reaction between bis( $\pi$ -allyl)nickel or -palladium halides and fluorophosphines RPF<sub>2</sub> (R = F, Me<sub>2</sub>N, Et<sub>2</sub>N).

In all cases irreversible transfer of the halogen atom from the metal to carbon readily occurs at room temperature or below to produce the appropriate allyl halide and the zerovalent metal fluorophospine complexes  $M(RPF_2)_4$ ,  $[M = Ni; R = Me_2N,$  $M = Pd; R = F, Me_2N, Et_2N].$ 

In the symmetrical  $\pi$ -allyl complexes the reactions are represented by Eqn. (1):



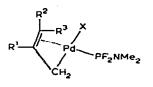
$$(M = Pd; R^{1} = H, CH_{3}; X = Cl; R = F, Me_{2}N, Et_{2}N)$$

We have investigated the intermediates in these processes by NMR spectroscopy both in above systems and the related 1-methylallyl- and 1,1-dimethylallylpalladium compounds where there are two possible modes of halogen migration to the terminal carbon of the allyl group.

Addition of small amounts of dimethylaminodifluorophosphine to (I) (M = Pd,  $R^1 = H$  or  $CH_3$ ) leads to the immediate establishment of a dynamic  $\sigma$ -allylic system up to molar ratios ligand/Pd between 1/1 and 2/1 followed by irreversible halogen migration from the metal to carbon. In the unsymmetrical 1-methyl- and 1,1-dimethyl- $\pi$ -allyl

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compounds the NMR spectra of the species in solution just prior to halogen migration are consistent with the existence of (II) and the complex (II) ( $R^1 = R^2 = H$ ,  $R^3 = CH_3$ , X = Br) has been isolated and characterised (Found C, 20.65; H, 3.77; N, 4.03.C<sub>6</sub>H<sub>13</sub>BrF<sub>2</sub>NPPd calcd.: C, 20.33; H, 3.67; N, 3.95%). Further addition of the fluorophosphine at  $-78^{\circ}$ affords the zerovalent palladium complex, 86% of the primary halide CH<sub>3</sub>CH=CHCH<sub>2</sub>Br and only 14% of the isomer CH<sub>2</sub>=CHCHBrCH<sub>3</sub>. Essentially the same isomer distribution is observed when the reaction is conducted at room temperature. The dimethylallyl complex (II) ( $R^1 = H$ ,  $R^2 = CH_3 = R^3$ ; X = Br) affords the primary halide (CH<sub>3</sub>)<sub>2</sub>C=CHCH<sub>2</sub>Br.



(II)  $(R^{1} = H, R^{2} = Me, R^{3} = H \text{ or } Me)$ 

Details of the changes observed in the <sup>1</sup>H NMR spectra of the  $\pi$ -allyl dimers on addition of the fluorophosphine ligands at various temperatures will be reported in full later<sup>11</sup>, but are comparable with the limited observations made in systems containing bis(2-methylallylpalladium chloride) and carbon monoxide<sup>10, 12</sup> where, however, evaporation of the solution regenerates the starting palladium dimer. The fluorophosphine induced migration of halogen mainly from the metal to the least substituted carbon atom parallels previous observations<sup>6-9</sup> on the insertion of carbon monoxide into palladium–carbon bonds in unsymmetrical allyl complexes. In the fluorophosphine reactions the ligand preferentially stabilises the zerovalent state of the metal and thus assists the transfer of the halogen atom from the  $\pi$ -allyl halogeno complex where the metal formally is in the divalent state. In analogous systems using carbon monoxide insertion of CO into the metal–carbon bond (allyl migration) may or may not precede halogen migration<sup>6-10</sup>. Studies on mixed carbonyl-fluorophosphine  $\pi$ -allyl-metal complexes are currently under way.

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