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# REACTIONS OF METHYL AND ETHYL HALIDES WITH THE COMPLEXES Ni[$P(C_2H_5)_3]_4$ AND Ni(X)[$P(C_2H_5)_3]_3$

A. MORVILLO and A. TURCO
*Centro C.N.R. Stabilità e Reattività Composti Coordinazione, University of Padova (Italy)*

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## Summary

The rates of the thermal reaction of the nickel(0) complex Ni[$P(C_2H_5)_3]_4$ with the alkyl halides $CH_3Br$, $CH_3I$ and $C_2H_5I$ in toluene have been compared with those of the reactions of the nickel(I) complexes Ni(X)[$P(C_2H_5)_3]_3$ (X = Br, I). The organic products from $CH_3X$ are methane and ethane, and those from $C_2H_5I$ are ethane and ethylene. The reactivity of the nickel(I) complexes is 10—20 times less than that of the nickel(0) complex. The results suggest that the first step of the reaction of nickel(0) with $CH_3I$ is the expected oxidative addition of the halide to the metal substrate. The intermediate thus formed decomposes to produce ethane (and small amounts of methane) without further reaction with the organic halide. This mechanism is supported by deuterium-labeling experiments.

## Introduction

The reactions of alkyl and aryl halides with nickel(0) complexes of the type $Ni(PR_3)_4$ have attracted considerable interest in recent years. Oxidative addition of the organic halides to the nickel(0) complexes or thermal decomposition of organometals $Ni(X)RL_2$ often involve nickel(I) complexes of the type $Ni(X)(PR_3)_3$. In some cases the nickel(I) complex can be isolated [1—4]. Alternatively, it may behave as a labile intermediate and react further with another alkyl halide [5,6]. The mechanism of the oxidative addition of the halides to nickel(I) complexes is of obvious interest, but studies involving the direct use of these complexes are scarce. In some cases [7] the reactions were studied by generating the nickel(I) species electrochemically in situ. Tsou and Kochi [4] report that the nickel(I) complex $Ni(X)(PEt_3)_3$ reacts with an excess of aryl halide in a reaction slower than that of $Ni(PEt_3)_3$, and is eventually converted into the nickel(II) complex $Ni(X)_2(PEt_3)_2$. We recently reported that the nickel(I) complex $[NiBr(PCy_3)_2]_2$ (Cy = cyclohexyl), (monomeric in solution) shows almost no reactivity towards alkyl halides, since it may be isolated as a product of the reaction of $Ni(PCy_3)_2$ with excess $C_2H_5Br$ after 18 hours at 20°C [8]. Thus the available information seems to suggest that the nickel(I) complexes $Ni(X)(PR_3)_n$ are less reactive towards alkyl halides than their potential precursors $Ni(PR_3)_n$. We report here the results of an investigation carried out with the principal aim of determining the relative reactivities of the two types of compounds towards alkyl halides.

## Results

### *Reactions of $CH_3I$ with $Ni(PEt_3)_4$ and $Ni(I)(PEt_3)_3$*

The reaction of $CH_3I$ with nickel(0) in toluene at 0°C was studied under pseudo first-order conditions (mole ratio 16 : 1) and was found to go to completion, producing 92% of ethane and 4.5% of methane (see Table 1). The logarithm of the difference between $x_\infty$ and $x_t$ (where $x$ represents the molar amount of liberated ethane) is plotted against time in Fig. 1. The semilogarithmic plot is curved, and can be separated into a fast and a slow component. The system was analyzed by the method of Francis and Jordan [9]. Extrapolation to zero time of the straight line portion of the slow reaction (broken line) gave the value of $x_\infty^{II}$, the moles of ethane liberated during the slow reaction (second step). The logarithm of $[(x_\infty - x_\infty^{II}) - x_t]$ was then plotted vs. time. The resulting straight line yielded a value of $14.8 \times 10^{-4}$ s$^{-1}$ for $k_{obsd}^{I}$, the pseudo first-order rate constant for the fast reaction (2.3 × slope). The straight line portion of the $\log(x_\infty - x_t)$ vs. time plot at longer times yielded $k_{obsd}^{II}$, the rate constant for the slow reaction ($k_{obsd}^{II} = 0.75 \times 10^{-4}$ s$^{-1}$).

The inorganic products isolated at the end of the first step consisted of equimolar amounts of $NiI(PEt_3)_3$ and the phosphonium salt $[PEt_3Me]I$. The amount of ethane liberated during the same reaction time corresponded to 0.5 moles of the gas per mole of reacted complex. The overall stoichiometry for the production of ethane during the first step conforms to the equation

$$Ni(PEt_3)_4 + 2\ CH_3I \rightarrow [PEt_3Me]I + NiI(PEt_3)_3 + \tfrac{1}{2}C_2H_6$$

The second step was found to proceed according to the stoichiometry

$$NiI(PEt_3)_3 + 2\ CH_3I \rightarrow [PEt_3Me]I + NiI_2(PEt_3)_2 + \tfrac{1}{2}C_2H_6$$

The reaction of $CH_3I$ with authentic samples of $NiI(PEt_3)_3$ gave the results shown in Fig. 2. The kinetic plot shows an induction period during which the rate of release of $C_2H_6$ is very small. Following the induction period the reaction proceeds with pseudo first-order kinetics. The value of the rate constant $k_{obsd}^{II}$ ($0.74 \times 10^{-4}$ s$^{-1}$) can be compared with the value determined from the second step of the reaction with $Ni(PEt_3)_4$ ($0.75 \times 10^{-4}$ s$^{-1}$) (Table 1).

In order to follow independently the rate of disappearance of $CH_3I$, the fast step of the reaction of nickel(0) was also studied using a lower concentration of the halide ($[CH_3I] = 0.1$, $[Ni(PEt_3)_4] = 0.05$). On addition of $CH_3I$ to the nickel(0) solution, an instantaneous change of colour from violet ($Ni(PEt_3)_3$) to yellow takes place. The reaction is complete in less than 50 seconds and involves the consumption of one mole of $CH_3I$ per mole of the nickel complex (Table 2). An additional mole of $CH_3I$ is consumed in a much slower reaction ($t_{1/2} = 3 \pm 0.5$

TABLE 1

RATE CONSTANTS FOR APPEARANCE OF HYDROCARBONS AND PRODUCT YIELDS IN THE REACTION BETWEEN ALKYL HALIDES AND NICKEL COMPLEXES

| Complex | Conc. (*M*) | Organic halide | Conc. (*M*) | $10^4 k_{\text{obsd}}$ [a] ($s^{-1}$) | Initial yields [b] | | | Product yields [c] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $CH_4$ | $C_2H_6$ | $C_2H_4$ | $CH_4$ | $C_2H_6$ | $C_2H_4$ |
| $[Ni(PEt_3)_4]$ | 0.048 | $CH_3I$ | 0.76 | 14.8 [d]<br>0.75 [e] | 0.05 | 0.95 | | 0.045 | 0.92 | |
| $[NiI(PEt_3)_3]$ | 0.048 | $CH_3I$ | 0.67 | 0.74 | | | | 0.03 | 0.41 | |
| $[Ni(PEt_3)_4]$ | 0.047 | $C_2H_5I$ | 0.75 | 4.03 [f]<br>1.76 [g] | | 0.30 | 0.70 | | 0.5 | 0.86 |
| $[NiI(PEt_3)_3]$ | 0.047 | $C_2H_5I$ | 0.66 | 0.29 [f]<br>0.15 [g] | | | | | 0.34 | 0.66 |
| $[Ni(PEt_3)_4]$ | 0.048 | $CH_3Br$ | 0.76 | | 0.05 | 0.95 | | 0.225 | 0.725 | |
| $[NiBr(PEt_3)_3]$ | 0.048 | $CH_3Br$ | 0.67 | | | | | 0.20 | 0.275 | |

[a] The accuracy for $k_{\text{obsd}}$ is estimated as ±7%. [b] Relative yields at the beginning of the reaction i.e. in the absence of hydrocarbons generated by nickel(I) complexes. [c] Mole/mole of complex; sum of the yields of the first and second step. [d] First step. [e] Second step. [f] Ethylene. [g] Ethane.

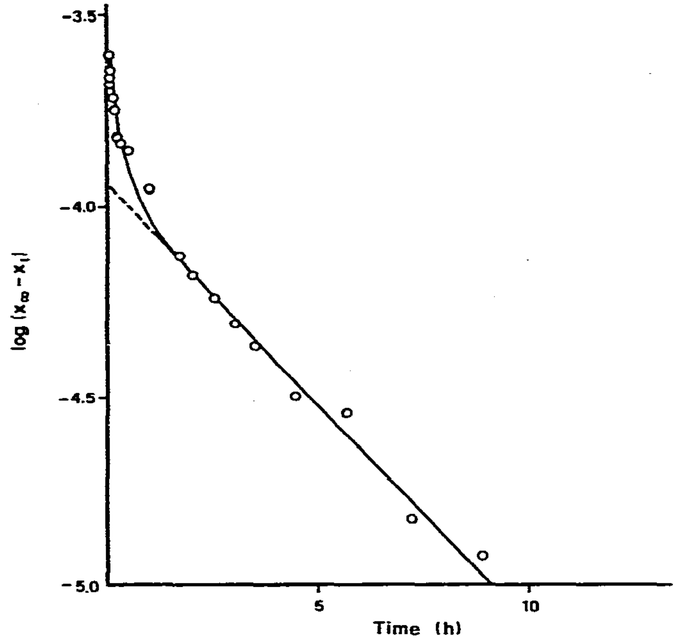

Fig. 1. Kinetic plot for the appearance of $C_2H_6$ from 5 ml of 0.048 *M* $Ni(PEt_3)_4$ reacting with 0.76 *M* $CH_3I$ in toluene at 0°C.

hours), which gives mainly phosphonium salt.

We also followed independently the appearance of ethane. From the plots of moles of ethane vs. time we were able to estimate an approximate value $t_{1/2}$ =

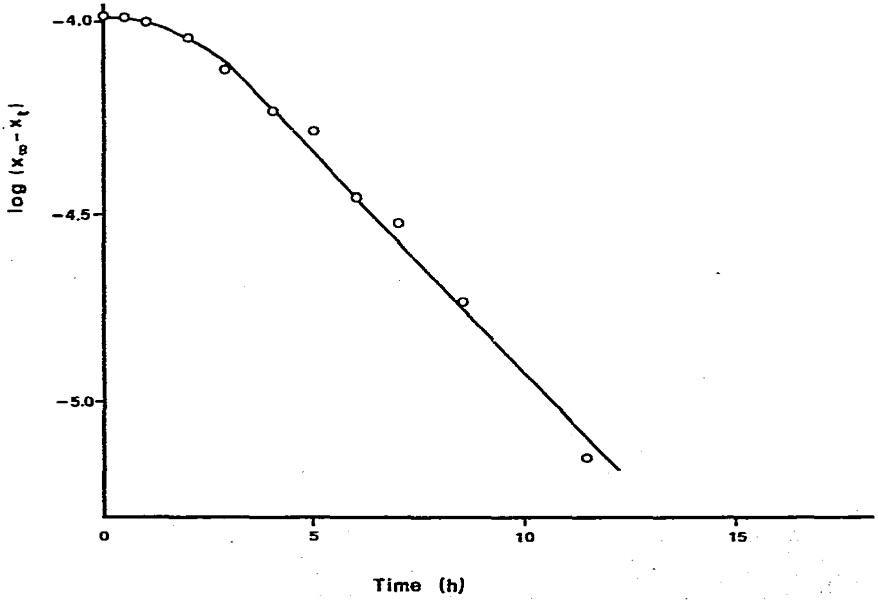

Fig. 2. Kinetic plot for the appearance of $C_2H_6$ from 5 ml of 0.048 *M* $NiI(PEt_3)_3$ reacting with 0.67 *M* $CH_3I$ in toluene at 0°C.

TABLE 2

RATES OF REACTION OF $CH_3I$ WITH NICKEL COMPLEXES

| Complex | $t_{1/2}$ [a] (s) | | |
|---|---|---|---|
| | Disappearance of $CH_3I$ [b] | Appearance of $C_2H_6$ | |
| $[Ni(PEt_3)_4]$ | <50 [c] | 420 [b] | 468 [d] |
| $[NiI(PEt_3)_3]$ | >39600 | 126 000 [b] | ~16 200 [e] |

[a] Measured from the kinetic curves; estimated error ±20%. [b] [complex] = 0.05, $[CH_3I]$ = 0.1. [c] Referred to the disappearance of the first mole of $CH_3I$. [d] [complex] = 0.048, $[CH_3I]$ = 0.76. [e] [complex] = 0.048, $[CH_3I]$ = 0.67 ($t_{1/2}$ includes the induction period).

420 seconds for the half-period of formation of the gas. *

The kinetics of disappearance of $CH_3I$ in the reaction with $NiI(PEt_3)_3$ are difficult to study because of the concurrent formation of the insoluble phosphonium salt, which takes place at a comparable rate. From the kinetic plots it was possible to estimate a value $t_{1/2} > 39\,600$ s for the half-period of disappearance of $CH_3I$ and $t_{1/2} = 126\,000$ s for the liberation of ethane (see Table 2).

### *Reaction of $Ni(PEt_3)_4$ with $CD_3I$*

The deuterium labeling studies were conducted by adding an equimolar amount of $CD_3I$ to a 0.05 *M* solution of $Ni(PEt_3)_4$ at 0°C in toluene. After one minute the same amount of undeuterated $CH_3I$ was added to the solution. The mixture was allowed to react for 10 minutes and the gaseous products were analyzed by GC/MS. The clean formation of $CD_3CD_3$ confirmed that the second mole of methyl iodide had not contributed to the formation of ethane.

In order to elucidate the mechanism of formation of methane, which is also generated in small amounts in the reaction of $Ni(PEt_3)_4$ with methyl iodide, a 0.05 *M* solution of the complex in $C_6D_5CD_3$ was allowed to react at 0°C with $CD_3I$ in 1 : 16 mole ratio. The mass spectrum showed that the gaseous products generated in the reaction were exclusively $CD_3CD_3$ and $CD_3H$. This result shows that the methane is formed by abstraction of hydrogen from the phosphine, and that no hydrogen comes from the solvent, and furthermore, it rules out the participation of the ethyl groups of the phosphines in the formation of ethane [10].

### *Reaction of $C_2H_5I$ with $Ni(PEt_3)_4$ and $NiI(PEt_3)_3$*

Ethyl iodide reacts with $Ni(PEt_3)_4$ in toluene at 0°C to produce ethylene, ethane and trace amounts of butane. Table 1 shows that the molar ratio of ethylene ($n_a$) to ethane ($n_b$) has a value of 2.33 at the beginning of the reaction, and falls gradually over at longer reaction times. The curves in Fig. 3 show how the yields vary with time. The semilogarithmic plot of ($x_\infty - x_t$) vs. time was linear

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* In this instance it was not possible to determine the value of the rate constants accurately. The rate study was not carried out under pseudo first-order conditions (small excess of $CH_3I$) and the reaction was too fast to allow accurate determination of initial rates.

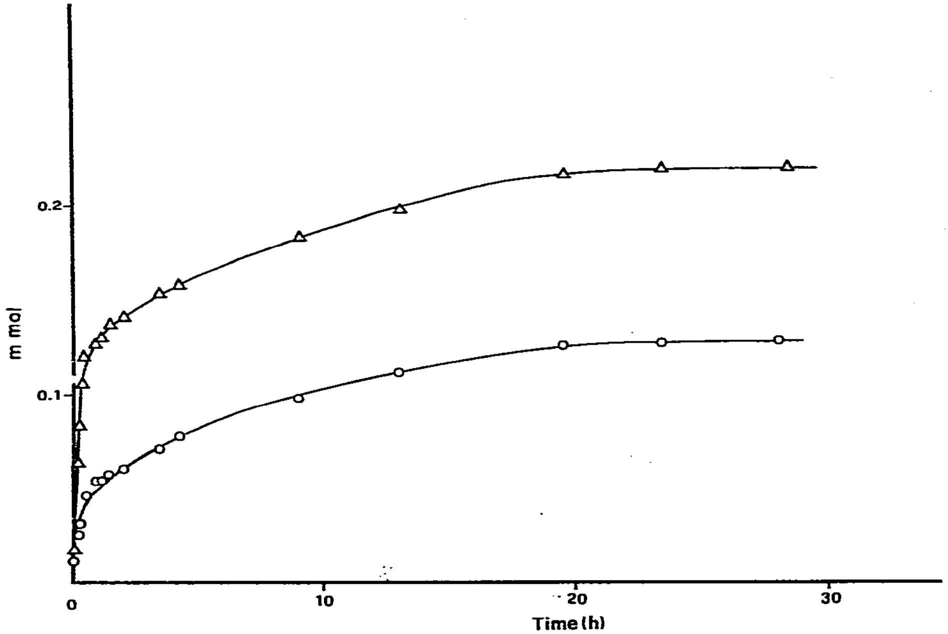
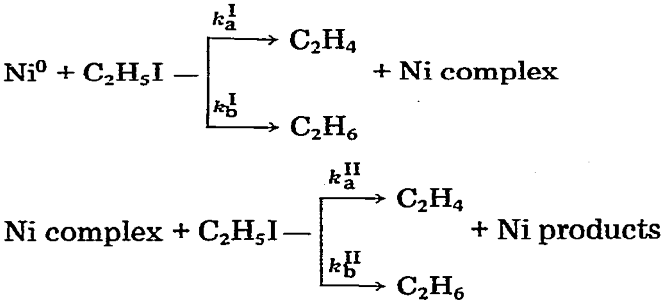


Fig. 3. Plot of the appearance of $C_2H_6$ (circles) and $C_2H_4$ (triangles) against time for the reaction of Ni$(PEt_3)_4$ with $C_2H_5I$ in toluene at 0°C. [complex] = 0.047; $[C_2H_5I]$ = 0.75.

for at least two half periods of the reaction, as shown in Fig. 4. * The rate data were analyzed in terms of a sequence of two consecutive steps, each producing ethylene and ethane according to Scheme 1.

SCHEME 1



$$Ni^0 + C_2H_5I \begin{cases} \xrightarrow{k_a^I} C_2H_4 \\ \xrightarrow{k_b^I} C_2H_6 \end{cases} + \text{Ni complex}$$

$$\text{Ni complex} + C_2H_5I \begin{cases} \xrightarrow{k_a^{II}} C_2H_4 \\ \xrightarrow{k_b^{II}} C_2H_6 \end{cases} + \text{Ni products}$$

For the first step the general rate law may be written as

$$-\frac{dA}{dt} = k^I A = (k_a^I + k_b^I)\,A \qquad (1)$$

where $k_a^I$ and $k_b^I$ are the observed rate constants for the appearance of ethylene and ethane, respectively, and $A$ the number of moles of the complex equivalent

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[*] It was assumed that one mole of complex produces one mole of gas (ethylene or ethane) by reacting with one mole of $C_2H_5I$ (see the discussion below). The symbol $x_\infty$ represents the total amount of gas (moles of ethylene plus ethane) produced during the first step.

Fig. 4.

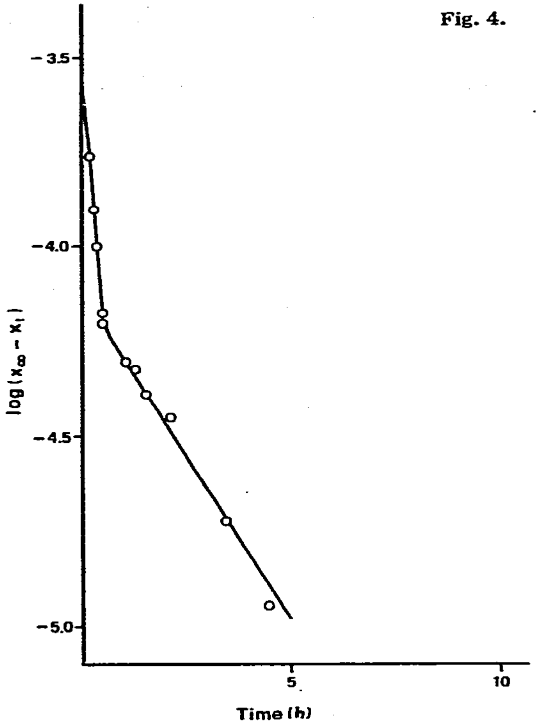

Fig. 5.

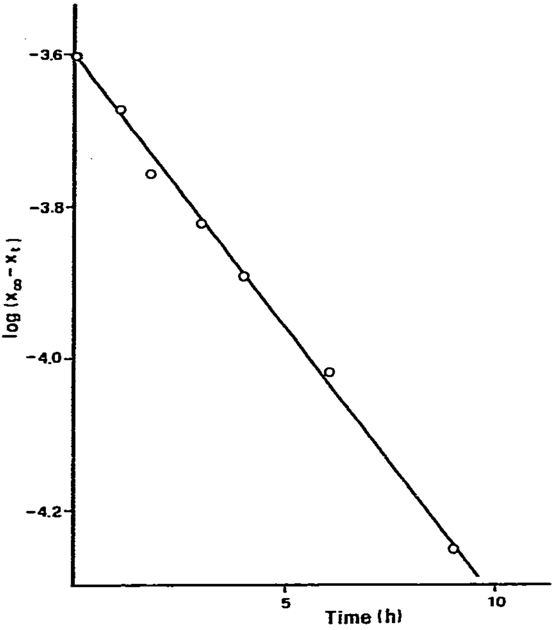

Fig. 4. Kinetic plot for the appearance of hydrocarbons ($C_2H_6 + C_2H_4$) in the reaction of 0.047 $M$ Ni($PEt_3)_4$ with 0.75 $M$ $C_2H_5I$ in 5 ml of toluene solution at 0°C.

Fig. 5. Kinetic plot for the appearance of $C_2H_6$ from the reaction of $NiI(PEt_3)_3$ (0.047 $M$) with $C_2H_5I$ (0.66 $M$) in 5 ml of toluene solution at 0°C.

to $x_\infty$. The fast portion (straight line) of the curve in Fig. 4 yielded the value $5.79 \times 10^{-4}$ $s^{-1}$ for the overall rate constant $k^{I}$. The values of the rate constants $k_a^{I}$ and $k_b^{I}$, determined from eq. 1 in conjunction with eq. 2,

$$\frac{k_a^{I}}{k_b^{I}} = \frac{n_a}{n_b} = 2.33 \qquad (2)$$

were $k_a^{I} = 4.03 \times 10^{-4}$ $s^{-1}$ and $k_b^{I} = 1.76 \times 10^{-4}$ $s^{-1}$ (Table 1).

The rates of reaction between ethyl iodide and authentic samples of $NiI(PEt_3)_3$ were studied under conditions similar to those above. Figure 5 shows that the value of $\log(x_\infty - x_t)$ is linearly related to time, indicating a pseudo first-order reaction. A treatment similar to that above yielded values of the rate constants for the evolution of ethylene ($k_a^{II} = 0.29 \times 10^{-4}$ $s^{-1}$) and ethane ($k_b^{II} = 0.15 \times 10^{-4}$ $s^{-1}$), respectively. As Table 1 shows, 100% yields of the hydrocarbons are produced from the reaction of nickel(I). It is noteworthy that under similar conditions the complete conversion of $Ni(PEt_3)_4$ (first plus second step) produces 1.37 moles of gas per mole of the complex.

### *Reactions of $CH_3Br$ with $Ni(PEt_3)_4$ and $NiBr(PEt_3)_3$*

The kinetic behaviour observed for the reactions between $Ni(PEt_3)_4$ and $CH_3Br$ was similar to that discussed for the reactions with $CH_3I$. The complex was found to react in two consecutive steps. The first step produced ethane, methane and the phosphonium salt $[PEt_3Me]Br$ along with an equimolar amount of $NiBr(PEt_3)_3$. The second, slower, step involved the reaction of $CH_3Br$ with $NiBr(PEt_3)_3$ as shown by the identity of the kinetic plots with those obtained with authentic samples of the nickel(I) complex. The amounts of ethane and methane liberated in the early stages of the first step were in the ratio 0.95 : 0.05. As can be inferred from Table 1, ethane and methane were liberated by the reaction of $NiBr(PEt_3)_3$ in the ratio 0.42 : 0.58. It is noteworthy that the yields reported in Table 1 for the reaction of $Ni(PEt_3)_4$ represent a satisfactory average of the single yields produced during the two steps.

## Discussion

To facilitate the discussion we first present the general mechanism for the reaction of nickel(0) and methyl iodide in Scheme 2 (where P = $PEt_3$ and RX = $CH_3I$).

SCHEME 2

$$NiP_4 \rightleftharpoons NiP_3 + P \qquad (3)$$

$$NiP_3 + RX \overset{\text{v.fast}}{\rightleftharpoons} Ni^{II}(X)(R)P_2 + P \qquad (4)$$

$$Ni^{II}(X)(R)P_2 \xrightarrow{\text{slow}} \left\{ \begin{array}{ll} \rightarrow RH + Ni^{II}\text{ complex} & (5) \\ \xrightarrow[+P]{} RR + Ni^{I}(X)P_3 & (6) \end{array} \right.$$

$$Ni^{I}(X)P_3 + RX \xrightarrow{\text{slow}} \text{intermediate} \left\{ \begin{array}{ll} \xrightarrow{\text{very}} RH + Ni^{II}\text{ complex} & (7) \\ \xrightarrow{\text{slow}} RR + Ni^{II}(X)_2P_2 & (8) \end{array} \right.$$

According to Scheme 2 the dissociation of $Ni(PEt_3)_4$ is followed by the reaction of one mole of $CH_3I$ with an equivalent amount of $Ni(PEt_3)_3$ to yield the oxidative adduct $NiI(CH_3)(PEt_3)_2$. This intermediate decomposes to produce small quantities of methane and equimolar amounts of ethane and $NiI(PEt_3)_3$. The nickel(I) complex reacts further with $CH_3I$ to produce methane and ethane, eventually giving an unreactive nickel(II) complex.

Each of the important steps of Scheme 2 will now be examined separately. It is known that oxidative additions to $NiP_4$ complexes take place by reaction of the dissociation products $NiP_3$ and $NiP_2$ [11,12]. Although the $NiP_2$ species are much more reactive than the 3-coordinate complexes it is reasonable to assume that the latter are effectively the sole reagents leading to $NiI(CH_3)(PEt_3)_2$. Formation of such an intermediate is strongly indicated by the observed instantaneous addition of $CH_3I$ to $Ni(PEt_3)_3$, which occurs without evolution of gas or of other decomposition products. This reaction is accompanied by the quaternization of free phosphine

$$Ni(PEt_3)_4 \rightleftharpoons Ni(PEt_3)_3 + PEt_3 \qquad (9)$$

$$Ni(PEt_3)_3 + CH_3I \xrightarrow{k_1} NiI(CH_3)(PEt_3)_2 + PEt_3 \qquad (10)$$

$$PEt_3 + CH_3I \rightarrow [PEt_3Me]I$$

The successive thermolysis of the intermediate may be depicted schematically as a bimolecular process

$$2\ NiI(CH_3)(PEt_3)_2 \xrightarrow[+2PEt_3]{k_2} 2\ NiI(PEt_3)_3 + C_2H_6 \qquad (11)$$

It is more likely however, that thermolysis and formation of the nickel(I) complex actually involve a sequence of successive reactions which we tentatively define as follows:

$$2\ NiI(CH_3)(PEt_3)_2 \rightarrow NiI_2(PEt_3)_2 + Ni(CH_3)_2(PEt_3)_2 \qquad (12)$$

$$Ni(CH_3)_2(PEt_3)_2 \xrightarrow{+PEt_3} Ni(PEt_3)_3 + CH_3CH_3 \qquad (13)$$

$$Ni(PEt_3)_3 + NiI_2(PEt_3)_2 \xrightarrow{+PEt_3} 2\ NiI(PEt_3)_3 \qquad (14)$$

Although speculative, such a thermolysis mechanism provides a reasonable explanation for the production of ethane along with the nickel(I) complex.

There is ample evidence for the first two steps occurring individually in aryl-derivatives, i.e. ligand exchange in eq. 12 and reductive coupling in eq. 13; eq. 14 represents the well known synproportionation of nickel(0) and nickel(II) [14].

We now discuss the results of the studies with $NiI(PEt_3)_3$. The induction period observed in the reaction with $CH_3I$ indicates that ethane is formed via some intermediate. Several interesting mechanistic possibilities can be invoked to interpret this result, including the formation of a fairly stable intermediate $NiI_2(CH_3)(PEt_3)_2$ by oxidative addition of $CH_3I$ to $NiI(PEt_3)_3$. However further studies are necessary to elucidate the nature of this intermediate.

Table 2 summarizes experiments which show that the rate of production of ethane is strongly dependent on the concentration of $CH_3I$ in the reaction with $NiI(PEt_3)_3$ but not in that with $Ni(PEt_3)_4$. This behaviour is consistent with the mechanism outlined in eqs. 10 and 11. If $k_1 >> k_2$ and the first step is very rapid this leads to a pseudo zero-order in $CH_3I$. The zero order situation is not encountered with $NiI(PEt_3)_3$ since in this case the rate of consumption of $CH_3I$ is comparable with that of liberation of $C_2H_6$. Finally, the data summarized in Tables 1 and 2 show that the reactivity of $NiI(PEt_3)_3$ is decidedly lower than that of $Ni(PEt_3)_4$, both in the oxidative addition and in the thermolysis.

The studies with $CD_3I$ in $C_6D_5CD_3$ demonstrate that the small amounts of methane liberated in the reaction of $Ni(PEt_3)_4$ are formed by abstraction of hydrogen from the ethyl groups of coordinated phosphines. An analogous mechanism was suggested previously for the reaction of $CD_3CN$ with $Ni(PCy_3)_2$. The reaction was found to produce exclusively $CD_3H$, showing that methane is formed by intramolecular abstraction of hydrogen from the phosphine ligands [15].

The reactions with methyl bromide conform to the pattern ascertained for the iodide, but there is a dramatic increase in the yield of methane as the complex is changed from nickel(0) to nickel(I) (from 5% to 42%, Table 1). Table 1 also shows that the relative yields are only slightly sensitive to variation of the complex in the reactions with methyl iodide and are not sensitive to variation of the halogen in the reactions with $Ni(PEt_3)_4$. Thus the main difference in the reactions of the two methyl halides resides in the differing importance of the thermolysis mechanisms (producing methane and ethane) involved in the reactions of the nickel(I) complexes. In particular, the absence of dependence of the yields on the halogen atom noted for the reactions of nickel(0) suggests that the competitive decomposition paths in eqs. 5 and 6 in Scheme 2 are kinetically insensitive to the halide (I, Br). These observations should be associated with our earlier conclusion that under thermolysis conditions the reaction of $Ni(PCy_3)_2$ with $CH_3CN$ affords methane, whereas ethane is the main product of the similar reaction with methyl iodide [15].

We finally comment briefly on the reactions of the nickel complexes with ethyl iodide. As expected, the reaction of $Ni(PEt_3)_4$ with $C_2H_5I$ differs from that with $CH_3I$ in three important ways: (a) the absence of reductive coupling processes (evidenced by the absence of butane), (b) the occurrence of $\beta$-elimination of hydrogen (producing ethylene); and (c) a diminished production of $NiI(PEt_3)_3$. We have made the reasonable assumption that one mole of nickel(0) or nickel(I) complex can produce one mole of gas (ethane plus ethylene) either by abstraction of hydrogen or by $\beta$-elimination. We now observe (Table 1) that authentic samples of nickel(I) produce one mole of gas per mole of complex. If the reaction of $Ni(PEt_3)_4$ with $C_2H_5I$ afforded exactly one mole of $NiI(PEt_3)_3$ we should expect a total yield of 2.0 moles of gas and not 1.37 moles as experimentally found. A reasonable explanation of this result is that the reaction of nickel(0) producing ethylene affords an hydrido complex of nickel(II) which does not lead to a species reactive towards $C_2H_5I$.

It should be noted that the rate constants obtained for the reaction between $C_2H_5I$ and the nickel(I) complex are ca. 10-fold lower than those obtained with the nickel(0) complex under the same conditions. Thus all the results summarized in Table 1 and Table 2 point consistently to the conclusion that the sequence of reactivity towards oxidative addition and thermolysis is nickel(0) > nickel(I).

## Experimental

### *General*

The solvent and the halides were obtained commercially and purified by standard methods. The complexes $Ni(PEt_3)_4$ [16], $NiBr(PEt_3)_3$ [1] and $NiI(PEt_3)_3$ [1] were prepared by literature methods. The solvents were distilled under argon before use. All reactions were carried out under argon in the dark. All the reactions were studied at 0°C. Mass spectra were recorded on a VG MM16F mass spectrometer equipped with a Dany 3800F chromatograph. GLC analyses were performed on a Perkin-Elmer Sigma 3B using a 2 m column packed with 5A molecular sieves, or a 2 m column packed with Poropak Q.

### *Product distributions and kinetic study*

Stock solutions of the complex reagent ($Ni(PEt_3)_4$ or $NiX(PEt_3)_3$ and of the appropriate organic compound RX in toluene were mixed in a closed vessel, which was placed in a thermostated bath. The concentration of the complex was $4.7$–$4.8 \times 10^{-2}$ *M* (see Tables 1 and 2). The concentration of the organic halides was $6.6$–$7.6 \times 10^{-1}$ *M* for the kinetic runs in Table 1, and $10^{-1}$ *M* for those in Table 2.

The progress of the reaction was followed by measuring the amount of gas evolved from 5 ml of the reacting solution. The determination of the gaseous products (methane, ethane, ethylene) was carried out by analyzing (GLC) known volumes of the gas phase in the reaction vessel. (Control runs were carried out to determine the amount of volatile products left in solution, and corrections were made for the amount of gas used in the uptake with the microsyringe.) The reproducibility and accuracy of the analytical method used was ±5%. In the runs in Table 2 the consumption of $CH_3I$ was also monitored by GLC using known volumes of the reagent solution. The inorganic products of the reaction of $Ni(PEt_3)_4$ with $CH_3Br$ or $CH_3I$ were isolated using the following procedure. Ten minutes after the reaction had started the excess of $CH_3I$ was rapidly pumped off under vacuum. The insoluble phosphonium salt $[PEt_3Me]X$ was filtered off and the resulting solution was reduced to a small volume under vacuum. After addition of light petroleum ether yellow crystals of $NiX(PEt_3)_3$ were precipitated out by cooling down to $-80°C$. An analogous procedure was used to isolate the inorganic products in the reaction of $NiI(PEt_3)_3$ with $CH_3I$. The phosphonium salt $[PEt_3Me]I$ was separated by filtration from the solution (after 30 hours of reaction). The resulting solution was reduced to a small volume under vacuum. The brown crystals which were precipitated by addition of ethanol gave an analysis corresponding to $NiI_2(PEt_3)_2$.

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