Journal of Organometallic Chemistry, 208 (1981) 103—113
Elsevier Sequoia S A., Lausanne — Printed in The Netherlands

REACTIONS OF ORGANIC HALIDES AND CYANIDES WITH BIS(TRICYCLOHEXYLPHOSPHINE)NICKEL(0)

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

(Received August 5th, 1980)

Summary

The reactions of the complex bis(tricyclohexylphosphine)nickel(0) ($Ni(PCy_3)_2$) with organic halides and cyanides RX ($R = CH_3$, $X = I$, CN; $R = C_2H_5$, $X = Br$, I, CN; $R = C_3H_7$, $X = Br$, CN; $R = C_6H_5$, $X = Cl$, CN), all involving fission of the R—X bond, have been studied in toluene at various temperatures. Oxidative addition of the bromides produces the stable complexes $[Ni^IBr(PCy_3)_2]_2$ and $Ni^{II}(H)(Br)(PCy_3)_2$. Methyl iodide affords phosphonium salts of a nickel(II) complex. The organic products of these reactions involve alkanes, alkenes, benzene, and reductive coupling products RR. Except for the methyl and phenyl derivatives the distribution of organic products is rather insensitive to the functional group X. The reactions are discussed in terms of molecular and radical mechanisms. The reactivity of $Ni(PCy_3)_2$ is compared with that of $Ni(PEt_3)_3$ and $Ni(PMe_3)_4$.

Introduction

The reactions of organo-halogen (or -pseudohalogen) compounds RX with low-valent metal complexes ML_m have been extensively investigated during the last ten years [1]. Oxidative addition of RX to ML_m, involving radical or molecular mechanisms can afford $M(X)(R)L_n$ as a stable adduct [2]. Alternatively, this compound can behave as a labile intermediate and decompose either by further reaction with excess RX [3], or by thermal decomposition. Hydrocarbons consisting mainly of alkanes (or arenes), alkenes and coupling products R—R are produced by the decomposition reactions. Molecular and/or homolytic mechanisms can both be involved in these transformations and lead to the same type of products. We recently found that CH_3CN reacts with $Ni(PCy_3)_3$ (Cy = cyclohexyl) in benzene at temperatures at which the expected product of the oxidative addition $Ni(CN)(CH_3)(PCy_3)_2$ decomposes to give CH_4 by intramolecular abstraction of hydrogen from the cyclohexyl groups [4].

0022—328X/81/0000—0000/$02.50, © 1981, Elsevier Sequoia S.A.

Homolytic formation of a $^{\cdot}CH_3$ radical could lead to the same result affording CH_4 by abstraction of hydrogen from the solvent.

The sequence of oxidative addition and elimination steps just described may be an alternative to other more straightforward decomposition pathways, which bypass the formation of the intermediate $M(X)(R)L_n$. For example, RX can decompose in one single homolytic step [5]:

$$ML_m + RX \xrightarrow{-L} M(X)L_n + R^{\cdot} \text{ etc.}$$

affording the same organic products produced by radical decompositions of $M(X)(R)L_n$ [6]:

$$M(X)(R)L_n \rightarrow M(X)L_n + R^{\cdot} \text{ etc.}$$

Thus, several mechanisms are available to account for the products observed from the decompositions of the organocompounds. In particular, Kochi had pointed out that a rigorous delineation of the mechanism is complicated by the dichotomy between molecular and homolytic processes [1].

The reactions of zerovalent d^{10} metal complexes have attracted considerable interest in recent years. Tsou and Kochi have interpreted the mechanism of the oxidative addition of aryl halides to the $Ni(PEt_3)_3$ complex in non radical terms [7]. Mechanisms based upon radical pathways have been presented for the majority of the decompositions of alkyl halides via oxidative additions to d^{10} metal complexes [2,5,6,8,9].

The system we chose for study is largely confined to the reaction of $Ni(PCy_3)_2$ with alkyl halides and cyanides. This system was selected mainly because, thanks to the low coordination number, the nickel complex shows a good reactivity towards the R—CN bond fission in aliphatic nitriles. Furthermore, some of the expected reaction intermediates ($Ni(X)(R)(PCy_3)_2$ [10], $[NiX(PCy_3)_2]_2$ [11], $Ni(X)(H)(PCy_3)_2$ [12]) are stable compounds and it was hoped that their isolation would facilitate the elucidation of the reaction mechanisms. Finally the intramolecular decomposition observed for the interaction of CH_3CN with $Ni(PCy_3)_3$ suggested that other reactions with $Ni(PCy_3)_2$ might proceed by an interesting non radical sequence of oxidative addition and elimination steps.

Results and discussion

A. Reactivity of phenyl compounds.

Tsou and Kochi [7] found that the oxidative addition of aromatic halides to $Ni(PEt_3)_3$ affords, in addition to the nickel(II) complex $Ni(Ar)(X)(PEt_3)_2$, the nickel(I) complexes $Ni(X)(PEt_3)_3$ as side products. The production of nickel(I) is accompanied by conversion of the aryl halide mainly to the corresponding

---

* The resulting solutions contained nickel(0) and tricyclohexylphosphine in 1.2 mol ratio (see experimental section). In formulating the complex as $Ni(PCy_3)_2$ we neglect equilibria involving the simultaneous existence in solution of species $Ni(PCy_3)$ and $Ni(PCy_3)_3$ [10].

arene according to the equation:

$$\mathrm{Ni(PEt_3)_3 + ArX \rightarrow Ni(X)(PEt_3)_3 + Ar^{\cdot}}$$

$$\mathrm{Ar^{\cdot} + SH \rightarrow ArH + S^{\cdot}}$$

In the present case, however, the main reaction path is provided by the decomposition of the intermediate $\mathrm{Ni(Ar)(X)L_2}$. As Table 1 shows, $\mathrm{C_6H_5Cl}$ reacts with $\mathrm{Ni(PCy_3)_2}$ giving biphenyl and minor amounts of benzene, in the same yields as observed for the thermal decomposition of $\mathrm{Ni(X)(C_6H_5)(PCy_3)_2}$ (X = Cl, Br). It is very unlikely that the coupling products observed are derived from a radical reaction of the type:

$$\mathrm{Ni(X)(C_6H_5)(PCy_3)_2 \rightarrow Ni(X)(PCy_3)_2 + {}^{\cdot}C_6H_5}$$

$$\mathrm{2\ {}^{\cdot}C_6H_5 \rightarrow C_6H_5C_6H_5}$$

Phenyl radicals, if formed, are expected to react rapidly by abstraction of hydrogen from toluene [13] to yield benzene and bibenzyl:

$$\mathrm{{}^{\cdot}C_6H_5 + C_6H_5CH_3 \rightarrow C_6H_6 + C_6H_5CH_2^{\cdot}}$$

$$\mathrm{2\ C_6H_5CH_2^{\cdot} \rightarrow C_6H_5(CH_2)_2C_6H_5}$$

However, no coupled bibenzyl was detected by gas-liquid chromatography of the reacting solutions.

It is now generally accepted [1,14] that reductive coupling processes take place through bimolecular mechanisms. Thus the almost exclusive formation of biphenyl is more easily accounted for in terms of a bimolecular reaction of the type [14]:

$$\mathrm{2\ Ni(X)(C_6H_5)L_\mathit{n} \rightarrow (C_6H_5)_2 + 2\ Ni(X)L_\mathit{n}}$$

An alternative explanation, based on the reaction [3]:

$$\mathrm{Ni(Ar)(X)(PR_3)_2 + 3\ ArX \rightarrow ArAr + [PR_3Ar]_2[NiX_4]}$$

can be ruled out, first because we did not observe formation of tetrahalonickelate salts and, second by the identity with the thermal decomposition of $\mathrm{Ni(Cl)(C_6H_5)(PCy_3)_2}$.

The striking similarity between the reaction of $\mathrm{C_6H_5CN}$ and the decomposition of $\mathrm{Ni(CN)(C_6H_5)(PCy_3)_2}$ (Table 1) leaves little doubt that the latter compound must be a reaction intermediate formed by oxidative addition of $\mathrm{C_6H_5CN}$ to $\mathrm{Ni(PCy_3)_2}$. This time benzene is the main product of the reaction, and one must think of an other mechanism, which must be much less important, if it operates at all, in the reaction with $\mathrm{C_6H_5Cl}$ discussed above. By analogy with the results with $\mathrm{CH_3CN}$ (vide infra) we are inclined to interpret the formation of $\mathrm{C_6H_6}$ in terms of intramolecular abstraction of hydrogen by $\mathrm{C_6H_5}$ from the cyclohexyl groups. Full elucidation of the mechanism would, however, require further investigation.

TABLE 1

PRODUCTS OF THE REACTIONS OF THE NICKEL COMPLEXES IN TOLUENE

Complex	Organic reagent	Conditions		Inorganic products (% yield) [a]	Organic products (% yield) [a]
		T (°C)	Time (h)		
$Ni(PCy_3)_2$	CH_3I	0	26		CH_4 (7), C_2H_6 (83)
	C_2H_5Br	0	26	$[NiBr(PCy_3)_2]_2$ (30); $Ni(II)(Br)(PCy_3)_2$ (40)	C_2H_4 (50), C_2H_6 (15), C_4H_{10} (4)
	C_2H_5Br	20	18	$[NiBr(PCy_3)_2]_2$, $Ni(II)(Br)(PCy_3)_2$	C_2H_4 (58), C_2H_6 (14)
	C_2H_5I	0	38		C_2H_4 (62), C_2H_6 (10)
	C_3H_7Br	0	24	$[Ni(Br)(PCy_3)_2]_2$ (35); $Ni(II)(Br)(PCy_3)_2$ (43)	C_3H_6 (68), C_3H_8 (12), C_6H_{14} (2)
	C_6H_5Cl	60	24		C_6H_6 (5), biphenyl (90)
	CH_3CN	60	36		CH_4 (80), C_2H_6 (1)
	C_2H_5CN	60	36		C_2H_4 (65), C_2H_6 (10)
	C_3H_7CN	60	36		C_3H_6 (67), C_3H_8 (3)
	C_6H_5CN	60	36		C_6H_6 (40), biphenyl (16)
$Ni(PEt_3)_3$	CH_3CN	60	40		(<2)
	C_2H_5CN	60	40		C_2H_6 (2), C_2H_4 (3)
$Ni(PMe_3)_4$	CH_3CN	60	40		(0)
	CH_3I	0	<0.5		C_2H_6 (85)
$Ni(Cl)(C_6H_5)(PCy_3)_2$	thermal decomposition	60	12		C_6H_6 (3), biphenyl (93)
$Ni(CN)(C_6H_5)(PCy_3)_2$	thermal decomposition	60	12		C_6H_6 (45), biphenyl (18)
$Ni(Br)(C_6H_5)(PEt_3)_2$	thermal decomposition	80			biphenyl [c]

[a] Based on the nickel(0) conversion. [b] See experimental section. [c] See ref. 14.

B. Reactivity of alkyl compounds

Table 1 shows that the pattern of reactivity of the methyl derivatives is remarkably different from that of the higher homologs. We shall discuss the methyl compounds later but point out here that the relatively easy decomposition path offered by β-elimination is precluded for these compounds and other reaction pathways must be followed. Table 1 shows that CH_3I gives mostly the coupling product C_2H_6.

In contrast, the main reaction product from C_2H_5X is ethylene (although the decomposition to alkane is still important). The higher homologs produce the corresponding alkene almost quantitatively. That formation of alkenes, and not hydrogenation or reductive coupling is the most important mode of reaction for the higher alkyls is also shown by the low dependence of the yields on the nature of the functional groups: bromides differ from cyanides only in that they react giving small amounts of coupling products which are not observed for the cyanides. The low tendency of nitriles to undergo this type of elimination may be due to strengthening of the alkyl—metal bond in $Ni(CN)(R)(PCy_3)_2$ intermediates. This would make reductive coupling more difficult independent of the bimolecular or homolytic character of the process [6], e.g.:

$$2\,M(X)(R)L_n \rightarrow 2\,M(X)L_n + 2\,R^\cdot$$

$$2\,R^\cdot \rightarrow RR$$

The inorganic product isolated during the early stages of the reactions with alkyl bromides was $[NiBr(PCy_3)_2]_2$ which was precipitated in a pure state by addition of n-hexane after concentration of the solution. The same procedure when carried out at the end of the reaction yielded a mixture of $[Ni(Br)(PCy_3)_2]_2$ and $Ni(H)(Br)(PCy_3)_2$. We did not detect measurable amounts of $Ni(Br)_2(PCy_3)_2$ in the product solutions. The last finding ruled out a radical chain process based on the reaction [8]:

$$NiBr(PCy_3)_2 + RBr \rightarrow Ni(Br)_2(PCy_3)_2 + R^\cdot$$

and is consistent with the ascertained inertness of $[Ni(Br)(PCy_3)_2]_2$ at the temperatures chosen for this study. Consequently, the only radical processes to be considered are those involving nickel(0) or nickel(II) complexes.

Alkyl halides may be implicated in the following radical processes leading to nickel(I) complexes [5,6].

$$Ni(PCy_3)_2 + RX \rightarrow Ni(X)(R)(PCy_3)_2 \tag{1}$$

$$Ni(X)(R)(PCy_3)_2 \rightarrow Ni(X)(PCy_3)_2 + R^\cdot \tag{2}$$

$$Ni(PCy_3)_2 + RX \rightarrow Ni(X)(PCy_3)_2 + R^\cdot \tag{3}$$

Further, free radicals may react with the complex $Ni(H)(Br)(PCy_3)_2$ produced by β-elimination from $Ni(Br)(C_2H_5)(PCy_3)_2$ according to eq. 9. In an alternative bimolecular pathway the hydrido complex may react with $Ni(Br)(C_2H_5)(PCy_3)_2$. Both processes would afford alkanes [1,2] as described in eqs. 4 and 5.

$$Ni(H)(Br)(PCy_3)_2 + {}^\cdot C_2H_5 \rightarrow NiBr(PCy_3)_2 + C_2H_6 \tag{4}$$

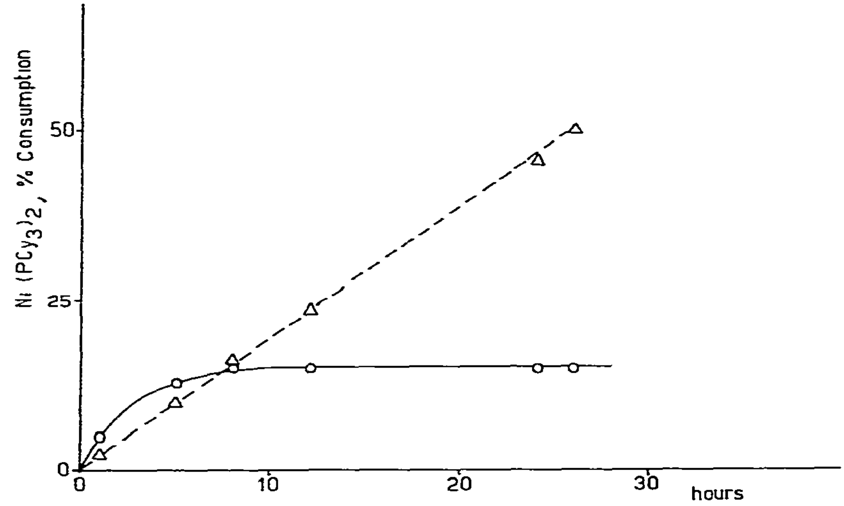

Fig. 1. Plot of the production of ethane (circles) and ethylene (triangles) against time. Concentrations: [Ni(PCy$_3$)] 10^{-1}, [C$_2$H$_5$Br] 1. Toluene solution, at 0°C.

$$\mathrm{Ni(H)(Br)(PCy_3)_2 + Ni(Br)(C_2H_5)(PCy_3)_2 \rightarrow 2\ NiBr(PCy_3)_2 + C_2H_6} \qquad (5)$$

Alkanes can also be produced by abstraction of hydrogen from the solvent or

$$\mathrm{{\cdot}C_2H_5 + {\cdot}C_2H_5 + C_6H_5CH_3 \rightarrow C_2H_6 + C_6H_5CH_2{\cdot}} \qquad (6)$$

from the cyclohexyl groups. A molecular counterpart of the latter process could involve a coordinate C$_2$H$_5$ group and cyclometallation [4] as illustrated in reaction 7:

$$\mathrm{L_nM(C_2H_5)P(C_6H_{11})_3 \rightarrow C_2H_6 + L_n\overline{MP(C}_6H_{10})(C_6H_{11})_2} \qquad (7)$$

Finally, alkanes can be produced by radical disproportionation and combination reactions

$$2\ {\cdot}\mathrm{CH_3CH_3} \begin{array}{l} \xrightarrow{k_c} \mathrm{CH_3CH_2CH_2CH_3} \\ \\ \xrightarrow{k_d} \mathrm{CH_2{=}CH_2 + CH_3CH_3} \end{array} \qquad (8)$$

We now discuss the relative importance of the reaction pathways described in eq. 1—9.

The absence of a products distribution in amounts dictated by the rate constants for combination (k_c) and disproportionation (k_d) of the ethyl radical (k_d/k_c for ethyl 0.185 in toluene [13]) rules out eq. 8 as an important mechanistic pathway. Furthermore, as Fig. 1 shows, there is no apparent correlation between the production of ethane and the yield of ethylene. Formation of the alkane is observed only in the early stages of the reaction and stops after a few hours. It also appears from Fig. 1 that ethane is initially produced in yields higher than ethylene. On the other hand the formation of ethylene is accompanied by that of $Ni(H)(Br)(PCy_3)_2$, indicating that the alkene is formed by β-elimination of hydrogen from $Ni(Br)(C_2H_5)(PCy_3)_2$, i.e.:

$$Ni(Br)(C_2H_5)(PCy_3)_2 \rightarrow Ni(H)(Br)(PCy_3)_2 + C_2H_4 \qquad (9)$$

In conclusion, the yields in Fig. 1 show that eq. 4 and 5 cannot represent the exclusive reaction pathways leading to ethane. They would require that the necessary hydridocomplex forms before ethane is produced. Our attention is thus directed to reactions 6 and 7 or related processes.

Despite intensive efforts we have been unable to obtain direct evidence for species produced by these reactions, such as bibenzyl (produced by coupling of benzyl radicals) or cyclometallated complexes. On the other hand the 15% yield of ethane must be consistent with the 30% yield of $[Ni(Br)(PCy_3)_2]_2$ to which it is strictly related. It is noteworthy that the reaction producing ethane goes rapidly to completion. Furthermore, the hydrido complex can be obtained only after the end of the production of ethane. From such observations we conclude that the reaction of the starting complex $Ni(PCy_3)_2$ proceeds via two independent but parallel pathways represented by eqs. 1 and 3, with 1 faster than 3. The ethyl group can then react according to eq. 4, 6 and 7 but more rapidly along the first pathway. The hydrido complex formed in reaction 9 is entirely consumed in the production of ethane and nickel(I) as long as there is still some $Ni(PCy_3)_2$ available for reaction 3.

As Table 1 shows, alkenes are the principal organic product of the reactions of $Ni(PCy_3)_2$ with alkyl halides and cyanides. We have interpreted the formation of the alkenes in terms of β-elimination from $Ni(Br)(C_2H_5)(PCy_3)_2$ (eq. 9). To prove the validity of this interpretation it is necessary to show that the formation of alkene is preceeded by the oxidative addition of RX to $Ni(PCy_3)_2$ (eq. 1). Alternatively, one can study the decomposition of the oxidative adduct $Ni(X)(R)(PCy_3)_2$. We have prepared solutions of $Ni(Br)(C_2H_5)(PCy_3)_2$ using the method of Jolly et al. [10] by addition of C_2H_5Br to toluene solutions of $Ni(PCy_3)_2$ (in 1/1 mol ratio) at −80°C, followed by slow warming to 20°C. No evolution of gas occurs during the stage of formation of the complex. The progress of this reaction was followed by monitoring the disappearance of the proton resonance peaks of C_2H_5Br. The subsequent decompositions were followed by GLC analysis of the gaseous phase in equilibrium with the solution. The reaction products (ethane, ethylene) and their yields were the same as those in the experiments at 0°C reported in Table 1. Repetition of the above procedure using a 10/1 mol ratio gave identical results. These findings confirmed in particular the correctness of the reaction scheme represented by eq. 8.

We shall now comment briefly upon the changes in the course of the reactions induced by the length of the alkyl chain of RX. A significant difference between the yields of alkanes and alkenes can be observed on comparing the reactions of ethyl and propyl compounds. This is not surprising since it is known that even small modifications in the nature of the alkyl group can have a profound influence on the course of the eliminations. For example, on going to dialkyl complexes the thermal decomposition of $(C_2H_5)_2Ni(bipy)$ liberates butane, whereas alkane and alkene in 1/1 ratio are produced from the n-propyl complex [15]. Obviously, much more important changes in the decomposition mechanisms are observed on going from ethyl to methyl derivatives [16]. For these latter compounds α-elimination is less feasible than reductive coupling or abstraction of hydrogen. Indeed, as Table 1 shows, the reaction of $Ni(PCy_3)_2$ with CH_3I affords principally ethane and produces only minor amounts of methane. Moreover, a dramatic change of mechanism is observed in the reaction with CH_3CN which, in contrast to CH_3I, gives methane.

The reaction of CH_3I is fast and only the final inorganic reaction product, a phosphonium salt of the type $[PCy_3Me][NiI_3(PCy_3)]$, could be isolated from the solution. Phosphonium compounds have sometimes been reported to be products of the oxidative addition of alkyl or aryl halides to d^{10} metal complexes [3,17,18]. In particular, it is known that addition of excess of CH_3I to a solution of Ni(Me)(I)P-i-Pr_3 in ether causes an immediate reaction at 0° C with precipitation of red crystals of $[PPr_3Me][NiI_3P\text{-}i\text{-}Pr_3]$ [19]. We are inclined to believe that a similar reaction occurs in the present case, but any attempt to interpret the results is complicated by the lack of information on reaction intermediates. The interest in the results with the methyl derivatives resides in the fact that they show how the reactions are influenced by the functional groups (iodide and cyanide). Table 1 shows that, by contrast, the organic product distributions with higher homologs are rather insensitive to the functional group (chloride, iodide, cyanide).

Also noteworthy is the strict analogy in the reaction products from methyl and phenyl derivatives. Indeed the low yields of alkane and benzene formed from CH_3I and C_6H_5Cl, respectively, indicate that hydrogen abstraction from solvent or alkyl groups in both cases competes only slightly with reductive coupling to R—R. We are inclined to interpret the last process more in terms of intermolecular reactions of $Ni(X)(R)(PCy_3)_2$ complexes than the radical reactions. The analogy between the reactions of methyl and phenyl compounds extends to the cyanide derivatives. As we have already noted in Section A, abstraction of hydrogen, to give hydrocarbons, becomes the competitive process for CH_3CN and C_6H_5CN.

We finally comment upon the reactions of the complexes $Ni(PMe_3)_4$ and $Ni(PEt_3)_3$. Table 1 shows that CH_3CN does not appreciably react with $Ni(PMe_3)_4$ at 60°C. By contrast CH_3I reacts very rapidly at 0°C affording C_2H_6 almost in 85% yield in less than half an hour. The enormous difference in rate indicates that different mechanisms are operative for bromides and nitriles. Our previous work on the oxidative addition of C_6H_5CN and CH_3CN to nickel(0) complexes [4,20] points to the conclusion that the nickel(0) substrate must be coordinatively unsaturated in order that the addition of the nitrile can occur. The lack of reactivity of $Ni(PMe_3)_4$ towards nitriles can be attributed to the virtual absence in solution of reactive species of low coordination number as a consequence of the exceptionally high stability of the 4-coordinate complex [21]. In contrast to $Ni(PMe_3)_4$, the complex $Ni(PEt_3)_4$ is largely dissociated in solution, where it behaves assentially as $Ni(PEt_3)_3$. Accordingly, the reactivity towards CH_3CN and C_2H_5CN (Table 1), although very modest, is appreciable at 60°C.

In conclusion, the order of reactivity $Ni(PCy_3)_2 > Ni(PEt_3)_3 > Ni(PMe_3)_4$ found for the aliphatic nitriles, is a further example [4,20,22] of the role played by coordinative unsaturation in determining the rates of processes requiring a preliminary oxidative addition step.

Experimental

Materials and procedure. Solvents and organic reagents (ethyl and propyl, bromide, methyl and ethyl iodide, methyl ethyl and propyl cyanide, phenyl chloride and phenyl cyanide) were obtained commercially and purified by standard methods. The complexes $Ni(PEt_3)_3$ [11] $Ni(CN)(C_6H_5)(PCy_3)_2$ [23] and $Ni(PMe_3)_4$ [24] were prepared by literature methods. Toluene solutions of bis(tricyclohexylphosphine)nickel were prepared by reducing $Ni(Br)_2(PCy_3)_2$ with sodium amalgam at 0°C by the previously described procedure [4].

The magnetic moments were measured by the Gouy method. Melting points were determined in sealed capillary tubes in vacuo and are uncorrected.

The solvents were distilled under argon prior to use. All reactions were carried out under argon in darkness. Reaction temperatures for the specified reagents were: nitriles, 60°C; bromides, 0 or 20°C; methyl and ethyl iodide, 0°C. The thermal decomposition of $Ni(CN)(C_6H_5)(PCy_3)_2$ and $Ni(Cl)(C_6H_5)(PCy_3)_2$ was studied at 60°C.

Chlorophenylbis(tricyclohexylphosphine)nickel. To a toluene solution (15 ml) of 1.5 g (2.4 mmol) of bis(tricyclohexylphosphine)nickel at 20°C was added 1.4 g (12.4 mmol) of chlorobenzene. The solution was stirred for 3 h, and the resulting yellow solid was filtered off, washed with light petroleum and dried in vacuo. Anal. Found: C, 68.5; H, 9.8; Cl, 4.9. $C_{42}H_{71}NiP_2Cl$ calcd.: C, 68.9; H, 9.76; Cl, 4.85%.

Analysis of the organic products. Stock solutions of $Ni(PCy_3)_2$ and of the appropriate organic compound RX in toluene were mixed in a closed vessel, and contained in a thermostatted bath, The progress of the reaction was followed by determining the amounts of hydrocarbons produced during the reaction. The determination of the gaseous products (hydrogen, methane, ethane, butane, ethylene, propene, butene) was carried out by analyzing (gas-liquid chromatography) known volumes of the gas phase in the reaction vessel (blank runs were carried out to determine the amount of volatile products left in solution). To determine less volatile products (benzene, n-hexane) the liquid material was completely transferred in vacuo from the reaction vessel to another flask prior to GLC analysis. Analyses of the biaryl (biphenyl, bibenzyl) were carried out by gas-liquid chromatography of samples of the reaction mixture, using a 2 m 15% Apiezon L column operating at 200°C. Preliminary tests confirmed the correctness of this procedure.

Figure 1 shows that bromoethane in toluene at 0°C, reacts with $Ni(PCy_3)_2$ to yield initially more ethylene than ethane. Further reaction causes a steady increase in the production of ethylene whereas the evolution of ethane slows down and eventually stops.

Isolation of inorganic products. (A) Reaction with ethyl bromide and n-propyl bromide. A solution containing 1.6 mmol of $Ni(PCy_3)_2$ and 16 mmol of the appropriate alkyl bromide was allowed to react for 5 h at 0°C. The resulting brown solution was filtered through a column of alumina, the filtrate was concentrated in vacuo, and hexane was added. This yielded 340 mg (circa 30%)

of a yellow crystalline product which analyzed for bromobis(tricyclohexylphosphine)nickel(I). Found: dec. 150°C (in vacuo); magnetic moment at 20°C, μ_{eff} 2.2 BM in agreement with the value reported for $[NiBr(PCy_3)_2]_2$ [11].

If the reaction is allowed to proceed for 26 h (instead of 5) at 0°C, the above procedure leads again to the isolation of a yellow product with identical decomposition temperature and elemental analysis as before, but with a different value for the magnetic susceptibility (μ_{eff} 1.63 BM at 20° C). The ^1H NMR spectrum at 25°C of a solution of this product in C_6H_6 showed the triplet hydride resonance at —23 ppm with J 77 Hz, characteristic of the Ni—H resonance in $Ni(H)(Br)(PCy_3)_2$ [12].

These data show that the product consisted of a mixture of $Ni(H)(Br)(PCy_3)_2$ (diamagnetic) and $[Ni(Br)(PCy_3)_2]_2$ approximately in 1/1 ratio, as calculated from the magnetic susceptibility *.

(B) Reaction with methyl iodide. Bis(tricyclohexylphosphine)nickel(0) (1.6 mmol) was allowed to react with 16 mmol of CH_3I in toluene (15 ml) at 0°C. The brown-red crystals which precipitated were filtered off, washed with n-hexane and dried under vacuum, to yield 1.5 g of an impure product (unsatisfactory C, H, P, I analyses), m.p. 190°C. All attempts to recrystallize this product were thwarted by its low solubility in suitable solvents. The product is decomposed by water, alcohols, acetonitrile, nitromethane, It is insoluble in benzene, toluene, n-hexane, ethyl ether. It is soluble in nitrobenzene to give fairly stable red solutions. The conductance of 10^{-3} M solutions in this solvent at 20°C was $\Lambda_M = 20$ ohm^{-1} cm^2 mol^{-1}, assuming a formulation as $[P(C_6H_{11})_3CH_3][NiI_3P(C_6H_{11})_3]$. This value is within the range expected for a 1/1 electrolyte. Anal. Found: C, 45.2; H, 7.3; I, 35.8; P, 6.0. $C_{37}H_{69}I_3P_2Ni$ calcd.: C, 43.7; H, 6.85; I, 37.5; P, 6.1%. The compound is slightly soluble in acetone and $C_2H_4Cl_2$. In the latter solvent it survives long enough (1 h) for measurement of its electrolytic conductance (30.8 Ω^{-1} cm^2 mol^{-1} at 20°C) and recording of its absorption spectra. Comparison of the electronic spectra (recorded with a Cary Model 14 spectrophotometer) in $C_2H_4Cl_2$ (10^{-3} M solution) with the published spectra of $[n\text{-}Bu_4N][NiX_3P(C_6H_5)_3]$ (X = Br, I) [26] shows that the compound belongs to the same class of pseudotetrahedral complexes of nickel(II) (characteristic absorption maxima at 1055 and 750 nm to be compared with the maxima at 1095 and 765 nm reported for $[n\text{-}Bu_4N][NiI_3P(C_6H_5)_3$ The magnetic moment of the compound at 294 K was calculated assuming the formulation $[P(C_6H_{11})_3CH_3][NiI_3P(C_6H_{11})_3]$. The value μ_{eff} 3.00 BM found for the compound is to be compared with the value 3.46 BM (at 300 K) published for $[n\text{-}Bu_4N][NiI_3P(C_6H_5)_3]$ [26].

Conductance, elemental analysis and spectral data support the conclusion that the product of the reaction with CH_3I presumably was an impure phosphonium salt containing nickel(II) in a pseudotetrahedral environment of three iodine and one phosphorus atoms. If the formulation is correct, the low value measured for the magnetic moment confirms that foreign diamagnetic components were present as an impurity in the isolated product. This was not further investigated.

---

* According to the literature [11,12] the compounds $[Ni(Br)(PCy_3)_2]_2$ and $Ni(H)Br)(PCy_3)_2$ have identical decomposition temperature (150°).

(C) Reactions with RCN (R = CH_3, C_2H_5, C_3H_7, C_6H_{13}). Several attempts to isolate intermediates or final reaction products were made, involving cooling of the reacting solutions, taking them to dryness and extracting the residue with different solvents, and concentration of the solution followed by addition of solvents; in all cases impure cyanide-phosphino complexes were obtained. These products were a mixture of various compounds which we were unable to separate. The infrared spectra of the solids obtained in the reactions with C_2H_5CN and $C_6H_{13}CN$ showed a band at 1870 ± 2 cm^{-1} which is attributed to the ν(M—H) stretching in $Ni(H)(CN)(PCy_3)_2$ [12].

Acknowledgment

We thank Mr. F. Bergamin for outstanding laboratory assistance.

References

1 J.K. Kochi, Organometallic Mechanisms and Catalysis, Academic Press, New York, 1978; Chapters 7, 12, 13, and ref. therein.
2 J.A. Osborn, Organotransition-Met. Chem., Proc. Jpn-Am. Semin., 1st, 1974 (1975).
3 T.T. Tsou and J.K. Kochi, J. Amer. Chem. Soc., 101 (1979) 7547.
4 G. Favero, A. Morvillo and A. Turco, Gazz. Chim. Ital., 109 (1979) 27.
5 D.R. Fahey and J.E. Mahan, J. Amer. Chem. Soc., 99 (1977) 2501.
6 C.A. Weston, A.W. Verstuyft, J.H. Nelson and H.B. Jonassen, Inorg. Chem., 16 (1977) 1313.
7 T.T. Tsou and J.K. Kochi, J. Amer. Chem. Soc., 101 (1979) 6319.
8 A.V. Kramer, J.A. Labinger, J.S. Bradley and J.A. Osborn, J. Amer. Chem. Soc., 96 (1974) 7145.
9 M.F. Lappert and P.W. Lednor, J. Chem. Soc. Chem. Commun., (1973) 948.
10 P.W. Jolly, K. Jonas, C. Krüger and Y.H. Tsay, J. Organometal. Chem., 33 (1971) 109.
11 M. Aresta, C.F. Nobile and A. Sacco, Inorg. Chim. Acta, 12 (1975) 167.
12 M.L.H. Green, T. Saito and P.J. Tanfield, J. Chem. Soc. A, (1971) 152.
13 K.U. Ingold in J.K. Kochi (Ed.), Free Radicals, vol. 1, Wiley, New York, 1973, p. 36ff.
14 G.W. Parshall, J. Amer. Chem. Soc., 96 (1974) 7832.
15 T. Yamamoto, A. Yamamoto, S. Ikeda, J. Amer. Chem. Soc., 93 (1971) 3350; 93 (1971) 3360.
16 See ref. 3 in cit. 8.
17 T.T. Tsou and J.K. Kochi, J. Amer. Chem. Soc., 100 (1978) 1634.
18 See ref. 21 in cit. 5.
19 M.L.H. Green and M.J. Smith, J. Chem. Soc. A, (1971) 639.
20 G. Favero, A. Morvillo and A. Turco, J. Organometal. Chem., 162 (1978) 99.
21 C.A. Tolman, Chem. Rev., 77 (1977) 313.
22 M. Foà and L. Cassar, J. Chem. Soc. Dalton Trans., (1975) 2572.
23 F. Favero, M. Gaddi, A. Morvillo and A. Turco, J. Organometal. Chem., 149 (1978) 395.
24 H.F. Klein and H. Schmidbaur, Angew. Chem. Internat. Edit., 9 (1970) 903.
25 F.A. Cotton, O.D. Faut and D.M.L. Goodgame, J. Amer. Chem. Soc., 83 (1961) 344.