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REACTIVITY OF $Ni(CO)[P(C_6H_5)_2(CH_2)_4P(C_6H_5)_2]_2$ WITH (π-ACIDIC) LEWIS BASES. AN EXAMPLE OF REVERSIBLE COORDINATION OF CARBON MONOXIDE TO NICKEL(0)

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Summary

The tetracoordinate nickel(0) complex $Ni(CO)(DPB)_2$ (DPB = 1,4 bis(diphenylphosphino) butane), I, reacts readily with tetracyanoethylene (TCNE) even in 1 : 1 molar ratio with displacement of CO and formation of the known π-olefinic complex Ni(DPB)(TCNE). Complex I reacts with fumaronitrile (FN) in a two step reaction, the final products being $Ni(CO)_2(DPB)$ and Ni(DPB)(FN); the initial product is the tetracoordinate species Ni(CO)(DPB-P)(FN), which provides an example of reversible coordination of CO to nickel(0).

Complex I reacts easily with $P(OR)_3$ (R = CH_3, C_2H_5, C_6H_5, o-C_6H_4-CH_3) with complete and controllable substitution of one DPB molecule per nickel atom. The rate depends markedly on the nature of the entering group.

The complex does not react with propio- or benzo-nitrile or with alkynes under ambient conditions.

Introduction

Monocarbonyl nickel(0) complexes of the type $Ni(CO)L_3$ (L = neutral ligand) are rare [1], and when L is a substituted phosphine the number of examples of such complexes is very small, while there is an extensive literature on the chemistry of tri- and di-carbonyl nickel(0) complexes, the coordination chemistry of monocarbonyl complexes is virtually unknown.

As a part of our research on the chemistry of diphosphino complexes of nickel(0) [2], we describe below the behaviour of the known tetracoordinate complex [2a] $Ni(CO)(P(C_6H_5)_2(CH_2)_4P(C_6H_5)_2)_2$ (I) towards a variety of (π-acidic) Lewis bases, i.e., cyanoalkenes, alkynes, phosphites and saturated nitriles, with emphasis on the cyanoalkenes and phosphites.

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The tetracoordinate nature of complex I was proposed on the basis of "the 16 and 18 electron rule" [3]. The notation DPB-P will be used to indicate a molecule of diphosphine acting as a monodentate ligand.

Experimental

Infrared spectra were recorded on a Perkin—Elmer 457 spectrophotometer. Wavenumbers cited are the means of at least ten independent measurements; they are accurate to ±2 cm^{-1} and reproducible to better than ±1 cm^{-1}. Gas chromatographic analyses were performed with a Hewlett Packard 5759 instrument.

The reactions and measurements were carried out under argon. The solvents employed for the preparation of $Ni(DPB)_2$ were dried by standard methods and distilled under argon. Dichloromethane, propionitrile and benzonitrile were C. Erba grade reagents and were used as received. Acrylonitrile (AN), phenylacetylene, 2-propyn-1-ol, trimethylphosphite, triethylphosphite, triphenylphosphite (Suchardt) were distilled under vacuum and stored under argon at 0°C. (Tri-*o*-tolyl)phosphite was prepared by a published method [4], and distilled twice under vacuum. Fumaronitrile (FN) and tetracyanoethylene (TCNE) (Schuchardt) were recrystallized from chlorobenzene. $Ni(DPB)_2$ and $Ni(CO)(DPB)_2$ were prepared as described earlier [2a,b]. $Ni(CO)(DPB)_2$ displayed a strong $\nu(CO)$ band at 1910 cm^{-1} (Nujol mull and benzene solution) or 1907 cm^{-1} (dichloromethane solution). CH_2Cl_2 solutions of this complex are stable for several hours if prepared and stored under an inert atmosphere, but decompose rapidly in air, giving diphosphine oxide and $Ni(CO)_2(DPB)$ as final products.

A qualitative comparison between the IR spectra (Nujol) of $Ni(DPB)_2$, DPB and $Ni(CO)(DPB)_2$ has been carried out; a series of bands which are present in the spectra of DPB and $Ni(CO)(DPB)_2$ and absent in that of $Ni(DPB)_2$ is listed in Table 1.

Reactions of I with cyanoolefins

Dichloromethane solutions of I (10^{-2} *M*, 15 ml) prepared in a three necked

TABLE 1

DETAILS OF BANDS PRESENT IN THE IR SPECTRUM OF DPB AND Ni(CO)(DPB)(DPB-P) AND ABSENT IN THAT OF $Ni(DPB)_2$ [a]

IR bands (cm^{-1})	DPB	Ni(CO)(DPB)(DPB-P)
3070	w	m
1405	m	w
1320	m	w
1305	m	m
1165	s	w
910	m	m
855	w	s
720	m	m

[a] m = medium and w = weak intensity.

50 ml flask were treated at 21°C ± 0.2 with AN, FN and TCNE in concentrations varying from 10^{-2} to 2×10^{-1} *M*. The IR spectra of solutions treated with AN show no evidence of reaction even after 24 h.

In contrast, FN reacts with I, the spectral changes being strongly dependent on the nature of the atmosphere over the reaction mixture. In one series of experiments, hereafter referred to as involving an "open system", the reagents were mixed in the 50 ml thermostatted vessel, and usually ten aliquots of 200 μl of solution were sucked off through a gas-tight rubber cap at appropriate intervals for recording of the IR spectrum in the region 2400—1600 cm^{-1}, the solution being kept vigorously stirred. In a second series of experiments, referred to as involving a "closed system", 200 μl of a thermostatted reaction solution prepared as previously indicated were put into a permanent IR cell (thermostatted in an "air thermostat" at 21°C ± 0.2) about 20 sec after addition of I to the solution of FN and the reaction was followed by keeping the cell in the "air thermostat" and exposing it to the IR light for no longer than 60 sec for each measurement.

Gas chromatographic analysis of the atmosphere over the reaction mixture in the open system allowed the determination of the CO evolved in the course of the reaction. In the reaction of I with TCNE the colour changed immediately to green then rapidly returned to yellow, and at the same time there was rapid displacement of ca. the 80% of CO present in I.

Reaction of Ni(DPB)(FN) with CO

With the same apparatus and procedures, proper amounts of $Ni(DPB)_2$ and FN were added to CH_2Cl_2 (30 ml) to give a 10^{-2} *M* solution of Ni(DPB)(FN) [2b]. The solution appeared to be stable for at least 3 h at room temperature and displayed a strong ν(CN) band at 2195 cm^{-1}. Under moderate stirring, the atmosphere over the solution was removed by a 5 sec evacuation (mechanical vacuum pump) and CO at 1 atm. was admitted into the vessel. IR spectra were recorded after 30 sec. By the same procedure CO was pumped off and argon readmitted above the reaction solution. The IR spectrum was again recorded. The rapidity of the evacuation led to a total concentration increase of the solutions due to solvent evaporation of ca. 20% for 3 cycles.

Reactions of I with phosphites

Suitable amounts of pure phosphites were added by means of a microsyringe to 10^{-2} *M* solutions of I. The progress of the reaction was followed by recording the IR spectra of the solutions at various times. The decrease of the absorbance of the 1907 cm^{-1} band of I and the growth of the ν(CO) bands of the products provided a convenient means for following the reaction.

The estimate of the conversion of I into Ni(CO)(DPB)($P(OPh)_3$) and Ni(CO)(DPB)($P(O\text{-}o\text{-tolyl})_3$) was based on the residual absorbance of I at 1907 cm^{-1} after a reasonably long reaction time.

It was concluded that I is quantitatively converted into Ni(CO)(DPB)($P(OMe)_3$) or Ni(CO)(DPB)($P(OEt)_3$). This was based on the following observations: Addition of fractions of a one molar proportion of pure ligand to a large volume of a 10^{-2} *M* solution of I (volume changes negligable) caused instantaneous positive shifts of the 1907 cm^{-1} ν(CO) band of I (only one ν(CO)

band is detectable), the shifts being more pronounced for higher phosphite additions. Addition of $P(OMe)_3$ or $P(OEt)_3$ in a one molar proportion to I produced a single ν(CO) band (at 1920 and 1915 cm^{-1}, respectively) and further addition of ligand up to 2—3 times in excess caused no further spectral change for some minutes.

Results and discussion

Reactions with cyanoalkenes

Solutions 10^{-2} *M* of I in CH_2Cl_2 display a strong ν(CO) band at 1907 cm^{-1}. When the solution is made 10^{-2} to 2×10^{-1} *M* in AN (ν(CN) 2235 cm^{-1}) no reaction takes place even in 24 h at ca. 20°C, as shown by the invariance of the IR pattern.

If the nickel(0) solution is made 10^{-2} to 10^{-1} *M* in FN a fairly rapid reaction takes place, as shown by complex spectral changes in the 2400—1600 cm^{-1} retion. The most significant spectral changes are reported in Fig. 1 and the relevant absorbance data are reported in Fig. 2. The spectra in Fig. 1 and the data in Fig. 2 refer to the reaction in a closed system. (See Experimental section.) The spectral data are interpreted in Scheme 1 and the features are as follows: (i) There is a continuous decrease in the intensity of the reactant band at 1907 cm^{-1} (I). The band disappears almost completely after ca. 20 min under the conditions of Fig. 1; (ii) Two bands appear at 2205 (Ni(CO)(DPB-P)(FN)) and 2195 cm^{-1} (Ni(DPB)(FN)) and their intensities increase with time. Their absorbance ratio changes very markedly with time as shown in Fig. 2. The increase of the 2205 cm^{-1} band parallels very closely the appearance of a strong band at 1997 cm^{-1} (Ni(CO)(DPB-P)(FN)); (iii) There is a slow growth of bands at 1995 and 1935 cm^{-1} ($Ni(CO)_2$(DPB)) and at the end of the reaction they have almost the same intensity. The final spectrum has bands at 2195, 1995 and 1935 cm^{-1} (Fig. 1).

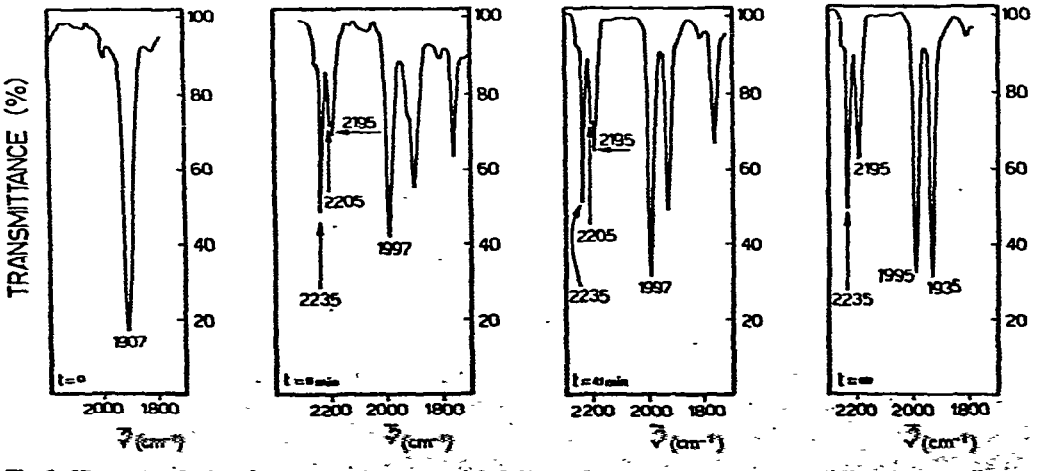


Fig. 1. IR spectra during the reaction between nickel(0) and fumaronitrile in CH_2Cl_2. "Closed system": $[Ni^0] = 10^{-2}$ M; $[CH_2{=}CHCN] = 20 \times 10^{-2}$ M; cell path = 0.5 mm.

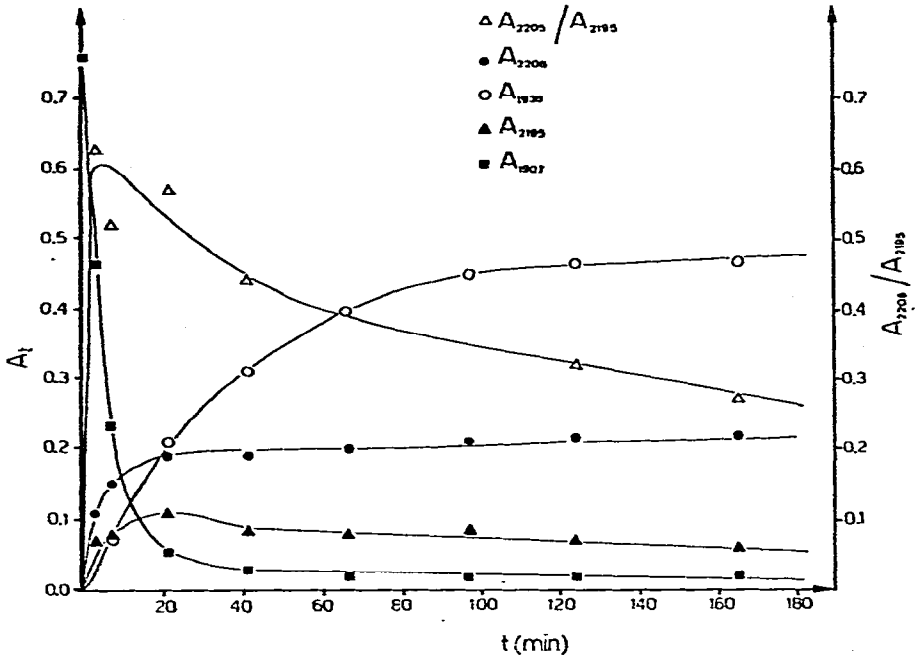
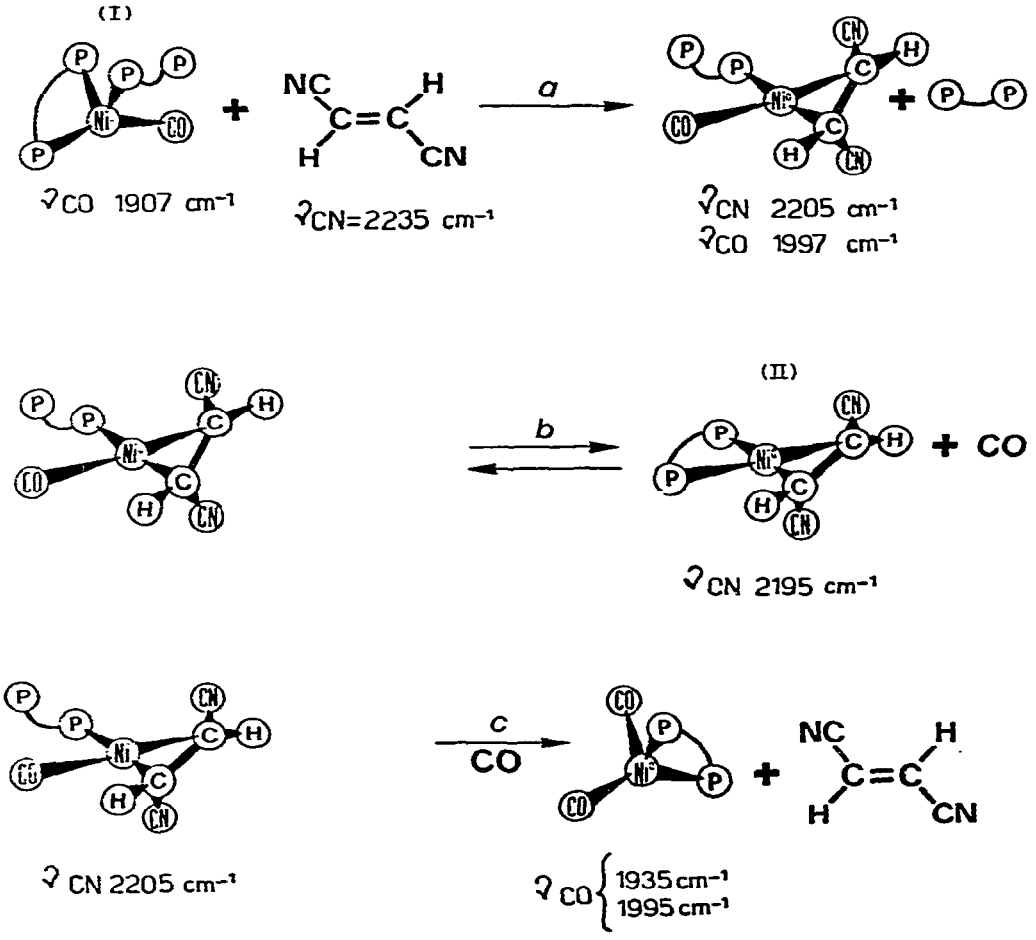


Fig. 2. Plots of absorbance at various wavenumbers versus time during the reaction between nickel(0) and fumaronitrile in CH_2Cl_2. "Closed system": $[Ni^0] = 10^{-2}$ *M*: $[CH_2{=}CHCN] = 20 \times 10^{-2}$ *M*: cell path = 0.5 mm.

It is important to note that the 1997 cm^{-1} band is well developed when the 1935 cm^{-1} band is only just appearing.

The spectral changes reported in Fig. 1, which refer to an FN concentration of 2×10^{-1} *M*, are very similar to those observed for lower FN concentrations, down to 10^{-2} *M*, the main difference being that the growth of the 2205 cm^{-1} band with respect to that at 2195 cm^{-1} is more marked at higher FN concentrations. Moreover, the rate of disappearance of the band at 1907 cm^{-1} increases with the FN concentration, indicating a clear concentration effect on the rate of consumption of I. The spectral changes and the rate of disappearance of the 1907 cm^{-1} band in the open system are very similar to those previously described, the major difference being that at all times the 2205 cm^{-1} band is far less intense than that at 2195 cm^{-1}. Moreover, the 1935 cm^{-1} band grows roughly three times as slowly as in the closed system.

Measurement of CO concentration in the atmosphere in equilibrium with the reacting solution (conditions as in Fig. 1, but with the open system) show that CO is a reaction product after only 2 min. (ca. 5% of the total CO originally coordinated to nickel(0)); its concentration reaches a maximum at ca. 15 min (ca. 60%), and decreases later, falling to a value corresponding to 30% after 400 min, when the IR spectrum of the solution displays the intense band at 2195 cm^{-1} (with a weak shoulder at 2205 cm^{-1} and the pair of bands at 1995 and 1935 cm^{-1} due to ($Ni(CO)_2(DPB)$).



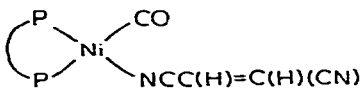
Steps a and b of Scheme 1 account for the formation of the species responsible for the 1997, 2195 and 2205 cm^{-1} bands. Equilibrium b which is considered to be fast, involves the reversible removal of CO from the coordination sphere of nickel(0). The complex Ni(DPB)(FN) (II) is a known species [2b], which can be prepared directly from $Ni(DPB)_2$ and FN in a 1 : 1 molar ratio. Carbon monoxide is thought to react with the primary product to give the known species $Ni(CO)_2$(DPB) [2a] and FN.

Step c is slower in the open than in the closed system as a consequence of the distribution of CO between the solution and the gas phase (CO is scarcely soluble in CH_2Cl_2).

The existence of steps b and c was demonstrated by reacting II with CO at [Ni] 10^{-2} *M* and P(CO) from 0.1 to 1 atm. The reaction leads to Ni(CO)(DPB-P)(FN) (bands at 1997 and 2205 cm^{-1}) and the reversibility of the CO coordination to the moiety Ni(DPB-P)(FN) was demonstrated by repeated removal of the atmosphere in equilibrium with II and Ni(CO)(DPB-P)(FN). This leads to

dramatic changes in the absorbance ratios of the bands at 2205 and 2195 cm^{-1}, in favour of the former under CO and to the latter under Ar. The number of coordination cycles of CO to nickel(0) was limited only by the irreversible reaction of Ni(CO)(DPB-P)(FN) with CO (step c).

The structure of the primary reaction product depicted in Scheme 1 is preferred to a possible alternative one, viz.:



This is because no ν(C=C) band was observed in the reaction mixture (apart from that of free FN) and only a single ν(CN) band attributable to coordinated FN, was detected. Moreover, the remarkable positive ν(CO) shift (+90 cm^{-1}) can be accounted for by the coordination to nickel(0) of a very strong π acceptor ligand ligand, which FN is. Finally, non-olefinic nitriles do not show any noticeable coordination ability to the Ni(CO)(DPB) moiety (see later).

When a 10^{-2} *M* solution of I is made 10^{-2} *M* in TCNE a very fast reaction occurs; the yellow solution immediately turns green and after few seconds again becomes yellow. The IR spectrum of the yellow solution displays a strong band at 2220 cm^{-1}, which can be attributed to the known species Ni(DPB)-(TCNE) (IV) [2b]. No coordinated CO appears to be present in the reaction mixture and 0.8 mol of CO per mole of nickel(0) were found in the atmosphere in equilibrium with the same solution.

The data are consistent with the occurrence of the overall reaction:

$$Ni(CO)(DPB)(DPB\text{-}P) + C(CN)_2{=}C(CN)_2 \rightarrow Ni(DPB)(C(CN)_2{=}C(CN)_2) + CO + DPB$$

which can be assumed to proceed through the primary adduct Ni(CO)(DPB-P)-(TCNE), which decomposes very rapidly and irreversibly to IV and free CO. (We have found that pure CO is totally unreactive towards 10^{-2} *M* CH_2Cl_2 solutions of Ni(DPB)(TCNE).)

The results for the cyanoalkenes investigated are remarkable in two respects. The first is that while all of them react easily with $Ni(DPB)_2$ to give the corresponding Ni(DPB)(alkene) species [2b] only FN and TNCE are reactive towards I. The second is that the alkene strongly labilizes the Ni—CO bond, and in the case of FN this leads to reversible coordination of one carbonyl ligand to nickel(0).

Reactions with phosphites

I reacts very easily at room temperature with $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$ and P(O-*o*-tolyl)$_3$. (A brief account of the reaction of I with $P(OPh)_3$ was published recently [5].) I reacts with $P(OPh)_3$ to give the complex Ni(CO)(DPB)(P-$(OPh)_3$) and the conversion is quantitative when a ten-fold excess of ligand is used ($[Ni^0] = 10^{-2}$ *M*).

If a 10^{-2} *M* solution of I is made equimolar in any of the phosphites, a very fast reaction takes place in the case of the alkyl phosphites, as shown by the immediate appearance of new single ν(CO) bands. Addition of P(O-*o*-tolyl)$_3$ causes a much slower change in the IR spectrum, the rate being similar to that

observed for the reaction with $P(OPh)_3$ [5], but the conversion into the substitution product proceeds only to an equilibrium (ca. 50% conversion).

Spectral and approximate kinetic data are collected in Table 2.

The spectral data in Table 2 are consistent with the occurrence of ligand substitution in I and the replacement of the coordination species ($P(C_6H_5)_2$-$(CH_2)_2$—) by the more π-acidic ligand $P(OR)_3$ [6]. We propose, therefore, that reaction of I with $P(OR)_3$ (1 : 1) leads quantitatively in the case of alkyl phosphites, and partially in the case of P(O-*o*-tolyl)$_3$ and $P(OPh)_3$ to the substitution product Ni(CO)(DPB)($P(OR)_3$).

The reversibility of the reaction of I with P(O-*o*-tolyl)$_3$ has been unambiguously demonstrated by adding free DPB (10^{-1} *M*) to the mixture at the end of the reaction (conditions as in Table 2), whereby the spectral changes observed during the direct reaction are slowly reversed while the isosbestic point is maintained.

Reaction of I with excess of $P(OR)_3$ leads to slow further substitution of DPB as shown by a further positive shift of the ν(CO) band. This aspect of the reaction of I with phosphites has not been investigated. It is noteworthy that no CO was displaced by any of the phosphites under any of the conditions we employed.

The outstanding feature of the data in Table 2 is that the rate of the substitution reaction is strongly dependent on the nature of the entering group. Thus $P(OMe)_3$ and $P(OEt)_3$ react roughly 10^2 times as fast as $P(OPh)_3$ or P(O-*o*-tolyl)$_3$, which could mean that a dissociative substitution mechanism, typical of nickel(0) complexes [7], does not operate.

While the kinetic results are somewhat surprising, the thermodynamic data are wholly consistent with the changes in the bulk of the ligands, as shown by their cone angles [8] ($P(OMe)_3$ 107° ± 2; $P(OEt)_3$ 109° ± 2; $P(OPh)_3$ 121° ± 10; P(O-*o*-Tolyl)$_3$ 165° ± 10).

Reactions with saturated nitriles and alkynes

I is unreactive toward propionitrile and benzonitrile and towards phenylacetylene and 2-propyn-1-ol. No changes in the IR were observed in solutions containing I (10^{-2} *M*) and the named reactants (10^{-2} to 10^{-1} *M*) for at least 24 h at room temperature.

We should point out that saturated nitriles are fairly good ligands towards the complex Ni(P(O-*o*-Tolyl)$_3$)$_3$ [9] and that the alkynes which are found to be

TABLE 2

SPECTRAL AND APPROXIMATE STOICHIOMETRIC AND KINETIC DATA FOR THE REACTION OF I WITH PHOSPHITES [a]

Phosphite	ν(CO) (cm^{-1})	t_{∞} (min)	conversion (%)
$P(OMe)_3$	1920	1	100
$P(OEt)_3$	1915	3	100
$P(OPh)_3$	1942	400	90
P(O-*o*-tolyl)$_3$	1942	2h	50

[a] [Ni] = 10^{-2} *M*; [$P(OR)_3$] = 10^{-2} *M*.

unreactive towards I react very easily with $Ni(DPB)_2$ [2b] to give the Ni(DPB) (alkyne) species.

Conclusions

The complex $Ni(CO)(DPB)_2$ discriminates sharply between reagents which are potentially good ligands towards nickel(0). While the higher reactivity of phosphites compared with saturated nitriles is not surprising, the very high reactivity of fumaronitrile and tetracyanoethylene towards I is in striking contrast with the non-reactivity of acrylonitrile and alkynes. The reason for this behaviour is probably related to the relative abilities of these Lewis bases to form strong covalent bonds to the moiety Ni(CO)(DPB). Apparently, saturated nitriles, which are rather poor π-acidic ligands, cannot compete successfully with the coordination entity $P(C_6H_5)_2(CH_2{-}CH_2{-})$ in I, while phosphites, known to be far better π acceptors than nitriles and DPB (the electronic properties of the latter should be similar to those of diphenylethylphosphine [6]) can readily do so.

As for the cyanoolefins and alkynes, it is important to point out that they have to break two Ni—P bonds, one of which belongs to a 7-membered ring and the product contains one DPB molecule per Ni atom which is forced to act as a monodentate ligand. This requires an exceedingly strong covalent synergic bond between Ni^0 and the olefins, and apparently only TCNE and FN are able to form such a bond.

TCNE and FN are known to be extremely good ligands towards metals in low oxidation states [10]. In particular in the reaction

$$Ni(P(O\text{-}o\text{-tolyl})_3 + \text{alkene} \overset{K}{\rightleftharpoons} Ni(P(O\text{-}o\text{-tolyl})_3)_2(\text{ene}) + P(O\text{-}o\text{-tolyl})_3$$

the value of K for FN is 3×10^3 times greater than that for AN at 25°C in benzene [11]. Moreover, it is also known [10] that acetylene, ethylene and AN are ligands of comparable bond ability, again in terms of equilibrium constants towards iridium(I). These facts taken together can explain our results and the failure of AN and the alkynes to react with I may be simply the result of their inability to form a sufficiently strong bond with nickel(0) to effect the breaking the special Ni—P bonds present in Ni(CO)(DPB)(DPB-P).

Noteworthy is weakening of the Ni^0—CO bond caused by TCNE and FN coordination to nickel(I) in the primary adduct Ni(CO)(DPB-P) (cyanoalkene). As a result, the carbonyl ligand is irreversibly displaced, in the first case, and becomes reversibly coordinated in the second. Other $Ni(CO)L_3$ complexes can probably display similar behaviour in their reactions with activated olefins and other examples of carbonyl ligand mobility are likely to be discovered.

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References

1 P. Jolly and G. Wilke, The Organic Chemistry of Nickel, Vol. 1, Academic Press, London, (1974).
2 (a) B. Corain, M. Bressan and G. Favero, Inorg. Nucl. Chem. Lett., 7 (1971) 197.

(b) B. Corain, M. Bressan and P. Rigo, J. Organometal. Chem., 28 (1971) 133.
(c) B. Corain, P. Rigo and G. Favero, Inorg. Chem., 10 (1971) 2329.
(d) B. Corain, Chem. and Ind., (1971) 1465.
(e) B. Corain and G. Puosi, J. Catal., 30 (1973) 403.
(f) B. Corain and G. Favero, J. Chem. Soc. Dalton, (1975) 283.
3 C.A. Tolman, Chem. Soc. Rev., 1 (1972) 337 and refs. therein.
4 Walsh, J. Amer. Chem. Soc., 81 (1959) 3023.
5 B. Corain and L. De Nardo, J. Organometal. Chem., 110 (1976) C27.
6 C.A. Tolman, J. Amer. Chem. Soc., 92 (1970) 2953.
7 P. Jolly and G. Wilke, The Organic Chemistry of Nickel, Vol. 1, Academic Press, London, 1974, p. 33.
8 C.A. Tolman, J. Amer. Chem. Soc., 92 (1970) 2956.
9 C.A. Tolman, Inorg. Chem., 10 (1971) 1540.
10 F.R. Hartley, Chem. Rev., 73 (1973) 164.
11 C.A. Tolman, J. Amer. Chem. Soc., 96 (1974) 2780.