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Carbon Monoxide Reaction towards Ni(II) Tetraco-ordinated Phosphine Complexes in Aqueous–Alcoholic Solution

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The Ni(II) tetraco-ordinated complexes of formula NiL_2X_2 *(X = Cl, Br; L =* PEt_3, PEt_2Ph, $PEtPh_2$*) react with CO in aqueous–alcoholic solution, to give Ni(0) carbonyls, via reductive carbonylation. The reduction has not been observed for L =* PPh_3*. The complexes* NiX_2*(diphos) {X = Cl, Br; diphos =* $[PPh_2]_2(CH_2)_n$*; n = 2,3} give reduction only in basic medium with partial oxidation of the ligand. A possible mechanism for the reductive carbonylation is discussed.*

Introduction

The increasing interest in the homogeneously catalysed water gas shift reaction for the possibility of increasing the hydrogen content in synthesis gas for practical applications (hydrogenation, hydroformilation, reduction of nitrobenzenes) [1], and our observation that complexes of nickel [2] can effectively catalyze the gas-shift reaction under mild conditions, prompted us to investigate the behaviour of some tetracoordinate complexes of formula NiL_2X_2 and $Ni(diphos)X_2$ [X = Cl, Br; L = PEt_3, PEt_2Ph, $PEtPh_2$, PPh_3; diphos = 1,2-bis(diphenylphosphino)ethane (dpe) and 1,3-bis(diphenylphosphino)prophane (dpp)] toward carbon monoxide in aqueous–alcoholic solution. Although the reduction of some complexes investigated by us has been already observed in both drastic [3] and mild conditions, the products of the reaction were not reported and the reducing species (carbon monoxide, phosphine, solvent) was not recognized.

The results obtained show that all the examined compounds, except complexes with PPh_3, are reduced to Ni(0). The reduction proceeds via reductive carbonylation for NiL_2X_2 complexes (eqn. 1).

$$Ni^{2+} + CO + H_2O \rightarrow Ni(0) + CO_2 + 2H^+ \qquad (1)$$

The $Ni(diphos)X_2$ are reduced both by CO and (partially) by phosphine. Our attempts to achieve the re-oxidation of Ni(0) complexes to Ni(II) to accomplish the catalytic cycle for the water gas shift have failed.

Results and Discussion

The Ni(II) tetraco-ordinated complexes of formula NiL_2X_2 (L = PEt_3, PEt_2Ph, $PEtPh_2$; X = Cl, Br) are reduced to Ni(0) under a carbon monoxide atmosphere in methanol or ethanol–water (5%) solution. The reduction is carried out at room temperature for PEt_3 and PEt_2Ph and at temperatures higher than 50 °C for $PEtPh_2$. The complexes with PPh_3 are unstable in the reaction medium, decomposing to NiX_2 and free ligand, and the reduction does not take place.

The determination of reaction products shows that the reduction of complexes proceeds via reductive carbonylation according to eqn. (2) followed by the equilibrium reaction (3):

$$NiL_2X_2 + 3CO + H_2O \rightarrow NiL_2(CO)_2 + 2HX + CO_2 \qquad (2)$$

$$NiL_2(CO)_2 + CO \rightleftharpoons NiL(CO)_3 + L \qquad (3)$$

The observation that carbon dioxide is the only gaseous product, the absence of phosphine-oxide and aldehyde (from alcoholic oxidation) in solution, and the lack of reduction in absolute methanol or ethanol, suggest that the carbon monoxide is the only reducing species. We observe also that the reduction is not quantitative because the nickel complexes are partially decomposed in aqueous–alcoholic solution. The decomposition (monitored by changes in the extinction coefficient of bands in the electronic spectrum of the NiL_2X_2 complexes) increases with increasing water percentage and decreases with increasing basicity of the phosphine.

Furthermore, the acidity developed in reaction (2) increases the decomposition of NiL_2X_2 complexes yielding salts of formula $NiX_4(LH)_2$ (reaction 4):

$$NiL_2X_2 + 2HX \rightleftharpoons NiX_4^{2-} + 2LH^+ \qquad (4)$$

These compounds, obtained from the reaction solution, after removal of a mixture of Ni(0) carbonyls with hexane, have been characterized by elemental analysis and comparison of their I.R. spectra with those of analytically pure samples obtained from NiL_2X_2 and HX in benzene solution. Their I.R.

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spectra display the P–H$^+$ stretching at 2435, 2430 and 2395 cm^{-1} respectively for PEt$_3$, PEt$_2$Ph and PEtPh$_2$ complexes. However when reaction (2) is carried out in the presence of free phosphine (phosphine/nickel ratio 1:2) or pyridine, the reduction is quantitative (Table I, runs 5, 6 and 12). The stoichiometry has been confirmed by gas-chromatographic determination of CO$_2$ and by titration of the acidity and unreduced Ni(II). The results listed in Table I show in fact that the CO$_2$ and the free acid are always obtained in the ratio 1:2. The amount of CO$_2$, which increases with the basicity of the ligand (Table I, runs 1, 8 and 14) as expected for the decreasing decomposition of the complexes, has been taken as a measure of the quantity of Ni(II) reduced. The free acid and the Ni(II) not reduced have been determined by titration with sodium methoxide or ethoxide (see Experimental). During the titration the pale-yellow carbonylated solution turned to red-violet, reaching a maximum when the total acidity was neutralised (first equiv. point). The electronic spectrum of the solution in this condition shows the presence of initial tetracoordinated Ni(II) complexes*. Their formation, due to a shifting to the left of the equilibrium (reaction (4)) by the added base, provides a further illustration of the influence that pyridine has on the progress of reduction. Also the di-tertiary phosphine complexes NiX$_2$(diphosph) are reduced by CO under ambient conditions (temperature and CO pressure) in aqueous alcoholic solution, but the reaction occurs only in the presence of the bases CH$_3$ONa, C$_2$H$_5$ONa or triethylamine. Furthermore in this case a small amount of phosphine-oxide has been obtained in addition to the carbon dioxide and Ni(0) carbonyls.

The phosphine oxide formation suggests that the familiar reduction of metallic ion by phosphine and water takes place partially (reaction 5):

$$M^{n+} + H_2O + L \rightarrow M^{(n-2)+} + 2H^+ + LO \qquad (5)$$

Support for this reaction is provided by the formation of Ni(0) complexes, Ni(dpe)$_2$ and Ni(dpp)$_2$, when the reaction with bases is performed under a nitrogen atmosphere and in the presence of free ligand. Using triethylamine, the reaction proceeds according to eqn. (6) which provides an alternative preparative route to those already known [5] for Ni(diphos)$_2$ complexes:

$$\text{NiX}_2(\text{diphos}) + 2\text{diphos} + 2\text{Et}_3\text{N} + \text{H}_2\text{O} \xrightarrow{N_2} \text{Ni(diphos)}_2 + \text{diphos-oxide} + 2\text{Et}_3\text{NHX} \qquad (6)$$

A possible mechanism for the reductive carbonylation is suggested in Scheme A:

TABLE I. CO$_2$ and HX Value after Reduction.

Run	Complex	Mmol	Time/h	Temp. 0 °C	Mmol CO$_2$^{a}	Mmol HX^b	% Ni reduced
1	NiBr$_2$(PEt$_3$)$_2$	0.37	3	R.T.	0.26	0.52	70
2	NiBr$_2$(PEt$_3$)$_2$	0.40	10	R.T.	0.28	0.56	71
3	NiBr$_2$(PEt$_3$)$_2$	0.49	20	70	0.35	0.70	71
4	NiBr$_2$(PEt$_3$)$_2$ + HCl (1:1)	0.36	15	R.T.	0.12	–	33
5	NiBr$_2$(PEt$_3$)$_2$ + Pyridine (1:6)	0.46	15	R.T.	0.46	–	100
6	NiBr$_2$(PEt$_3$)$_2$ + PEt$_3$ (1:2)	0.51	15	R.T.	0.50	–	98
7	NiCl$_2$(PEt$_3$)$_2$	0.45	5	R.T.	0.32	0.64	71
8	NiCl$_2$(PEt$_2$Ph)$_2$	0.36	5	R.T.	0.18	0.37	50
9	NiCl$_2$(PEt$_2$Ph)$_2$	0.37	15	R.T.	0.19	0.37	51
10	NiCl$_2$(PEt$_2$Ph)$_2$	0.37	15	70	0.20	0.41	54
11	NiBr$_2$(PEt$_2$Ph)$_2$	0.35	5	R.T.	0.18	0.36	51
12	NiBr$_2$(PEt$_2$Ph)$_2$ + PEt$_2$Ph (1:2)	0.50	20	R.T.	0.50	–	100
13	NiBr$_2$(PEtPh)$_2$	0.35	18	R.T.		–	–
14	NiBr$_2$(PEtPh)$_2$	0.31	18	70	0.074	0.15	24
15	NiCl$_2$(dpe)	0.35	20	70		–	–
16	NiCl$_2$(dpe) + Et$_3$N	0.40	20	R.T.	0.28	–	70
17	NiBr$_2$(dpe) + Et$_3$N	0.35	20	R.T.	0.26	–	74
18	NiBr$_2$(dpp)	0.40	20	70	–	–	–
19	NiBr$_2$(dpp) + Et$_3$N	0.38	20	R.T.	0.28	–	74

^{a}From gas-chromatographic measurements. ^{b}From potentiometric titrations.

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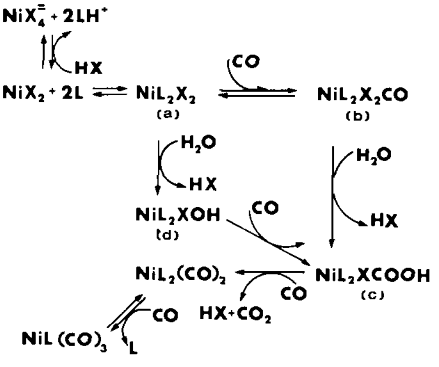
*The absorption spectra in the region 375–900 nm display bands at 394 and 536 ; 374 and 496; 372 and 494; 860, 496 and 380 nm respectively for NiBr$_2$(PEt$_3$)$_2$, NiCl$_2$(PEt$_3$)$_2$, NiCl$_2$(PEt$_2$Ph) and NiCl$_2$(PEtPh$_2$)$_2$.



Scheme A.

A labile carboxylic acid complex NiL_2XCOOH (C), which rearranges to give the Ni(0) complex and CO_2 is considered the key intermediate. Two possible routes are depicted leading to its formation: the first by nucleophilic attack of a water molecule on a pentaco-ordinate carbonyl NiL_2X_2CO (b) [4], and the second by initial formation of a hydroxy complex $NiL_2X(OH)$ (d) which undergoes CO-insertion to produce (C). Monitoring the reaction by I.R. spectroscopy we observe only the CO stretching absorptions of $NiX_2L_2(CO)$ at 2018, 2025, 2030 cm^{-1} respectively for $L = PEt_3$, PEt_2Ph, $PEtPh_2$ and $X = Br$.

The intensity of the carbonyl band remained constant with time in absolute ethanol but decreased in an ethanol–water mixture. The decreasing intensity of this band was accompanied by the appearance of two new bands between 1998–1990 cm^{-1} [9a,b, 10] and between 1940–1935 cm^{-1} [9a,b, 10] due to $NiL_2(CO)_2$.

A further band at 2065 cm^{-1} accompanied by a decreasing intensity of the lower frequency band of $NiL_2(CO)_2$ and broadening of the higher implied finally the formation of $LNi(CO)_3$.

Also, no spectroscopic evidence was obtained for the carboxylate complex $L_2NiX(COOH)$. However, hydroxy–carbonyl complexes postulated in the catalysis of the water gas shift reaction have been isolated only in a few cases [6]. Recently $(PEt_3)_2$-$PtCl(COOH)$ [7] analogous to the Ni-complex postulated here has been obtained by nucleophilic attack of a water molecule on the cationic carbonyl $[(PEt_3)_2PtClCO]^+$.

In the nickel case instead only the parent alkoxycarbonyls of formula $\{[Ni(PPhMe_2)_2(C_6Cl_5)(COOR)], R = CH_3, C_2H_5\}$ [8], $\{[(Ni(pnp)Cl(COOR)], R = CH_3\}$* and $\{[Ni(PEt_3)_2Cl(COOR)], R = CH_3, C_2H_5\}$* have been obtained by nucleophilic attack of alkoxide ions on a coordinated carbonyl group.

Experimental

All solvents were of reagent grade quality and were distilled and stored under a nitrogen atmosphere. Gas chromatographic determinations were carried out on Porapack Q column using a Carlo Erba Fractovap C connected to a Hewlett-Packard 3380 A integrator. Infrared spectra were recorded on a Perkin Elmer 577 spectrophotometer and electronic spectra on a Varian Cary 219. Potentiometric titrations were carried out on a Potentiograph E 336 Metrohom-Herisau. Complexes and ligands were prepared according to the literature methods.

Aldehyde and Phosphine-oxide Analysis

The absence of aldehyde was established by GLC analysis using a 20 M capillary column. The presence or absence of phosphine oxide was confirmed by i.r. spectroscopy: the spectra of the reaction mixtures, after carbonylation, were compared with those obtained from solutions containing the same complexes, after oxidation with molecular oxygen.

Carbonylation and CO_2 Analysis

All reactions were carried out in a glass-vessel reactor (60 ml) provided with a jacket for thermostatting. In a typical experiment 0.200 g (0.44 mmol) of $NiBr_2(PEt_3)_2$ were added to 10 ml of an ethanol–water (5%) solution under CO. The resulting red-brown solution was stirred until it became pale yellow (time 4 h, see Table I). At the end of the reaction the pressure in the reactor vessel decreased and CO, N_2 or argon was added to restore atmospheric pressure. The CO_2 produced was then quantitatively analysed by gas chromatography and the results corrected for the solubility of CO_2 in ethanol–water solution.

Titration of the Solution

All the titrations were carried out under a nitrogen atmosphere**. Typically a known quantity of reaction solution was diluted to 10 ml with ethanol and titrated, after which nitrogen was bubbled through the cooled solution to remove the CO_2 dissolved. The titration curves show two equivalent points corresponding to the total acidity (H^+ and R_3PH^+) for the first, and to the Ni(II) unreduced, for the second. The assignment is obtained by comparison with the relative curves obtained from solutions containing pure complexes with and without a known quantity of hydrochloric acid.

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*Experiments in progress.

**Exposure of solution to the air causes the oxidation of Ni(0) to Ni(II) and diminution of acidity (unpublished work).

Carbonylation of NiL_2X_2 giving Products (i) Ni(0) Carbonyls and (ii) $NiX_4(LH)_2$

Carbonylation of $NiCl_2(PEt_3)_2$ and $NiBr_2(PEt_3)$

0.500 g of $NiX_2(PEt_3)_2$ (X = Cl, Br) was carbonylated in 10 ml of ethanol–water (5%). The pale yellow solution was evaporated to dryness under vacuum and the resulting mixture gave a blue-green residue after extraction with hexane.

(*i*) The I.R. spectrum of the hexane solution displayed carbonyl stretching modes at 2065, 1990, 1930 cm^{-1}, assignable to a mixture of the known complexes $Ni(CO)_3PEt_3$ [12a,b] and $Ni(CO)_2(PEt_3)_2$ [12a,b]. An identical I.R. spectrum was shown by solutions obtained by reducing the $NiX_2(PEt_3)_2$ (X = Cl, Br) with sodium under carbon monoxide.

(*ii*) The blue-green residue was washed with a benzene–acetone mixture (4:1), dried, and analyzed as $NiCl_4(PHEt_3)_2$ or $NiBr_4(PHEt_3)_2$. *Anal.* Found: Ni, 13.2; P, 14.0; Cl, 32.5. Calcd. for $C_{12}H_{32}Cl_4NiP_2$: Ni, 13.38; P, 14.13; Cl, 32.32. Found: Ni, 9.4; P, 9.9; Br, 52.4. Calcd. for $C_{12}H_{32}Br_4NiP_2$: Ni, 9.53; P, 10.06; Br, 51.86.

$NiCl_4(PHEt_3)_2$ was also obtained as blue-green crystals by bubbling HCl gas through a benzene solution of $NiCl_2(PEt_3)_2$. *Anal.* Found: N, 13.3; P, 14.1; Cl, 32.4.

Carbonylation of $NiCl_2(PEt_2Ph)_2$ and $NiBr_2(PEt_2Ph)_2$

0.700 g of $NiX_2(PEt_2Ph)_2$ (X = Cl, Br) was carbonylated in 15 ml of ethanol–water (5%) solution. After reaction, the solution was evaporated to dryness and the resulting product mixture was fractionated with hexane under nitrogen atmosphere.

(*i*) The hexane solution contained the two carbonyls $Ni(CO)_3PEt_2Ph$ and $Ni(CO)_2(PEt_2Ph)_2$ as indicated by I.R. absorption bands at 2065, 1990 and 1932 cm^{-1} [12b, 13]. On cooling to -78 °C and after vigorous stirring, a white-cream product precipitated (45%) which was identified as $Ni(CO)_2(PEt_2Ph)_2$ by elemental analysis and I.R. spectrum. I.R. (nujol) 1990(vs), 1930 cm^{-1}. *Anal.* Found: Ni, 12.9; P, 13.5. Calcd.: $C_{22}H_{30}NiO_2P_2$: Ni, 13.14; P, 13.88.

An identical compound (I.R. and analysis) was obtained from the reaction of $NiCl_2(PEt_2Ph)_2$ with sodium in toluene solution under carbon monoxide.

(*ii*) The blue-green residue insoluble in hexane, was washed as reported above, dried and analysed. *Anal.* (for the product deriving from $NiCl_2(PEt_2Ph)_2$: Ni, 11.1; P, 11.3; Cl, 26.7. Calcd. for $C_{20}H_{32}Cl_4NiP_2$: Ni, 10.98; P, 11.60; Cl. 26.52. This product was also obtained by reaction between $NiCl_2(PEt_2Ph)_2$ and HCl as reported above.

Carbonylation of $NiCl_2(PEtPh_2)_2$ and $NiBr_2(PEtPh_2)_2$

0.500 g of $NiX_2(PEtPh_2)_2$ (X = Cl, Br) in 15 ml of ethanol–water (5%) was stirred under carbon monoxide at 70 °C. The dark-green starting complex slowly dissolved on reaction with CO. After 20 h, a white-cream microcrystalline product precipitated (15%) on cooling the solution.

(*i*) This product is formulated as $Ni(CO)_2(PEtPh_2)_2$ [13] on the basis of I.R. spectrum and analysis. I.R. (nujol) 1995(vs), 1930(vs) cm^{-1}. *Anal.* (%) Found: Ni, 10.7; P, 11.2. Calcd. for $C_{30}H_{30}NiO_2P_2$: Ni, 10.82; P, 11.42. The compound was also prepared from $NiCl_2(PEtPh_2)_2$ and Na under CO.

(*ii*) The aqueous–alcoholic solution was evaporated to dryness; the resulting mixture after washing with benzene gave blue-green $NiCl_4(PEtPh_2)_2$ or $NiBr_4(PEtPh_2)_2$.

Carbonylation of $NiCl_2(PPh_3)_2$ and $NiBr_2(PPh_3)_2$

0.500 g of $NiX_2(PPh_3)_2$ (X = Cl, Br) was suspended in ethanol–water (5%) under CO. After 2 h the greenish solution was evaporated to dryness leaving a mixture of the starting complex $NiX_2(PPh_3)_2$, NiX_2 and the free ligand. Performing the reaction in dry ethanol at 70 °C for four days gave only traces of $Ni(CO)_2(PPh_3)_2$.

Carbonylation of NiX_2(diphos)

$NiCl_2$(dpe) and $NiBr_2$(dpe)

0.500 g of $NiX_2[(PPh_2)CH_2]_2$ (X = Cl, Br) was suspended in 10 ml ethanol–water (5%) solution under CO and stirred at room temperature in the presence of 0.5 ml of triethylamine. After the suspension had turned from red-brown to pale yellow (5 h), the aqueous–alcoholic solution was evaporated *in vacuo*. The resulting residue was extracted with benzene and the extract evaporated to dryness. On standing in ethanol the resulting oil, a pale yellow crystalline product, was obtained and was identified as $Ni(CO)_2$dpe [14] by I.R. and analysis. The residue insoluble in benzene was analysed as Et_3NHX (X = Cl, Br).

$NiBr_2$(dpp)

0.500 g of $NiBr_2$(dpp) was reacted under conditions described for NiX_2(dpe) and the resulting products were identified as $Ni(CO)_2$dpp [15] and Et_3NHBr by analyses and I.R. spectra.

Preparation of Ni(diphos)$_2$

Ni(dpe)$_2$

0.264 g (0.50 mmol) of $NiCl_2$(dpe) and 0.400 g (1.0 mmol) of dpe ligand was suspended under a nitrogen atmosphere in 15 ml ethanol (95%). A solution of CH_3ONa (1 *M*) was added with stirring dropwise (molar ratio $CH_3ONa/Ni = 2.5$). The resulting yellow suspension was evaporated to dryness under vacuum and the residue extracted with benzene. The yellow $Ni(dpe)_2$ (80%) was obtained on adding ethanol to the concentrated benzene solution. *Anal.* Found: Ni, 6.9; P, 14.1. Calcd. for $C_{52}H_{48}$-NiP_4: Ni, 6.87; P, 14.51.

Ni(dpp)$_2$

This compound was prepared from 0.315 g (0.5 mmol) of $NiBr_2(dpp)$ and 0.412 g (1.0 mmol) of ligand dpp using the procedure described above. *Anal.* Found: Ni, 6.7; P, 13.9. Calcd. for $C_{54}H_{52}$-NiP_4: Ni, 6.65; P, 14.05.

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