

New Tetra- and Pentacoordinate Nickel(I) Complexes

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Summary

The reduction of nickel(II) halides with NaBH_4 in ethanol has been studied in the presence of various tertiary phosphines and arsines. Complexes of the type XNiL_3 have been isolated in this way when $X = \text{Cl, Br, I}$ and $L = \text{PPh}_3, \text{AsPh}_3$, no reaction being observed when $L = \text{PEt}_3, \text{PBu}_3$ and $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$.

The reaction of XNiL_3 with CO gas at room temperature produces pentacoordinate carbonyl complexes $\text{XNi}(\text{CO})_2\text{L}_2$ when L is triphenylphosphine. The lack of stability prevents the isolation of similar complexes when L is triphenylarsine.

Structural data obtained by i.r. spectroscopy and susceptibility measurements as well as chemical behaviour of the new complexes are described.

Introduction

We were interested in isolating nickel(I) complexes in order to use them in additions with $\text{BrFl}(\text{C}_6\text{F}_5)_2$ as a method for obtaining halo(pentafluorophenyl)nickel(II) complexes⁽¹⁾.

The first nickel(I) complexes were prepared⁽²⁾ by boiling $[(\pi\text{-allyl})\text{NiX}]_2$ in norbornene in the presence of triphenylphosphine. The method presents several disadvantages such as the low yield and the necessity of isolating the intermediate $\pi\text{-allyl}$ derivative.

A new simpler way was latterly described⁽³⁾ making use of the reduction of nickel(II) halides with NaBH_4 in the presence of triphenylphosphine.

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Here we report the results obtained in reactions with various ligands such as triphenylphosphine, triethylphosphine, tributylphosphine, 1,2-bis-diphenylphosphineethane and triphenylarsine and the behaviour of XNiL_3 complexes in substitutions with CO.

We have also extended our study to substitutions of XNiL_3 and $\text{XNi}(\text{CO})_2\text{L}_2$ complexes, here described, with 1,2-bis-diphenylphosphineethane as well as substitutions of X by several anions.

The results of these reactions will be published in a forthcoming paper.

Results and Discussion

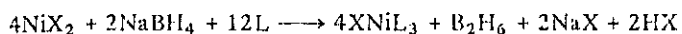
Preparations

When a freshly prepared solution of NaBH_4 in ethanol is added to ethanol solutions of hydrated nickel(II) halides containing triphenylphosphine or triphenylarsine in an exact $\text{BH}_4^-:\text{Ni}:\text{L}$ 1:2:6 molar ratio, the initially green or reddish solutions turn red (PPh_3) or yellow (AsPh_3) with simultaneous precipitation of a crystalline solid. The analytical composition of these solids agrees with that expected for the nickel(I) complexes (1-6) formulated in Table 1. No change was observed when the ligands added were triethylphosphine, tributylphosphine or an equimolar mixture of 1,2-bis-diphenylphosphineethane with any one of the mentioned tertiary phosphines and arsine.

So, in accordance with the following equation:

Table 1. Physical properties and analytical data for nickel(I) complexes

Complex	Colour	M.p. Dec (°)	Found (Calcd.)%			
			C	H	X	Ni
1 $\text{ClNi}(\text{PPh}_3)_3$	red	160	73.25 (73.5)	5.9 (5.1)	4.1 (4.0)	7.0 (6.7)
2 $\text{BrNi}(\text{PPh}_3)_3$	red	147	71.7 (70.1)	4.9 (4.8)	8.5 (8.6)	5.7 (6.3)
3 $\text{INi}(\text{PPh}_3)_3$	red	150	66.4 (66.6)	4.75 (4.6)	13.0 (13.05)	6.0 (6.0)
4 $\text{ClNi}(\text{AsPh}_3)_3$	yellow	124	63.3 (64.0)	4.1 (4.4)	(3.5)	5.7 (5.8)
5 $\text{BrNi}(\text{AsPh}_3)_3$	yellow	130	61.2 (61.3)	4.1 (4.25)	7.5 (7.6)	5.3 (5.55)
6 $\text{INi}(\text{AsPh}_3)_3$	yellow	160	58.3 (58.7)	4.2 (4.1)	11.3 (11.5)	4.8 (5.3)
7 $\text{ClNi}(\text{CO})_2(\text{PPh}_3)_2$	pale green	155	67.6 (67.6)	5.1 (4.4)	5.0 (5.3)	8.5 (8.7)
8 $\text{BrNi}(\text{CO})_2(\text{PPh}_3)_2$	green	159	64.1 (63.4)	4.2 (4.2)	11.2 (11.1)	8.4 (8.2)
9 $\text{INi}(\text{CO})_2(\text{PPh}_3)_2$	red	179	60.8 (59.5)	4.0 (3.9)	16.1 (16.6)	7.45 (7.7)



sodium borohydride reduces nickel(II) to the tetracoordinate nickel(I) complexes XNiL_3 , where $\text{X} = \text{Cl}, \text{Br}, \text{I}$ and $\text{L} = \text{PPh}_3, \text{AsPh}_3$.

All the complexes (1-6) are stable under nitrogen at room temperature in the solid state. They decompose in the air, becoming green. The decomposition is almost instantaneous in chloroform with disproportionation to give green solutions containing nickel(I), the free ligand and a grey insoluble residue.

Passage of CO gas at room temperature through suspensions of complexes (1-3) in ethanol produces a weakening of the initial red as crystalline complexes (7-9) respectively precipitate. The analytical composition of these compounds corresponds to the stoichiometries formulated in Table 1.

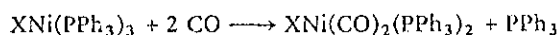
The carbonyl complexes (7-9) are stable at room temperature in the solid state and they are unchanged by air for long periods. They are soluble in organic solvents such as chloroform and benzene but their solutions evolve CO and immediately, turning green, so that recrystallization is not possible.

The same reactions with complexes (4-6) give pale yellow crystalline solids which rapidly decompose on filtration, thus preventing the isolation of similar triphenylarsine carbonyl derivatives. The green solid residue obtained in all cases does not contain CO.

Table 2. Magnetic and i.r. for nickel(I) complexes

Complex	$\chi_M \cdot 10^6$	$\mu_{\text{eff.}}$ (B.M.)	$\nu(\text{Ni-X})$ (cm^{-1})	$\nu(\text{C}\equiv\text{O})$ (cm^{-1})
1 $\text{ClNi}(\text{PPh}_3)_3$	1726	2.0	295	
2 $\text{BrNi}(\text{PPh}_3)_3$	1892	2.1	—	
3 $\text{INi}(\text{PPh}_3)_3$	1693	2.0	—	
4 $\text{ClNi}(\text{AsPh}_3)_3$	2035	2.2	—	
5 $\text{BrNi}(\text{AsPh}_3)_3$	1561	1.9	—	
6 $\text{INi}(\text{AsPh}_3)_3$	1760	2.0	—	
7 $\text{ClNi}(\text{CO})_2(\text{PPh}_3)_2$	2048	2.2	335	1996-1930
8 $\text{BrNi}(\text{CO})_2(\text{PPh}_3)_2$	1704	2.0	—	
9 $\text{INi}(\text{CO})_2(\text{PPh}_3)_2$	1854	2.1	—	

Probably, decomposition takes place in the same way as with the triphenylphosphine complexes whose lack of solubility in ethanol prevents their decomposition. In accordance with the equation:



the reactions with CO produce not only substitution of triphenylphosphine but also increase in coordination number from four to five. This behaviour agrees with the known tendency⁽⁴⁾ of metal atoms to expand their coordination sphere by introduction of CO.

Magnetic Moments

The room temperature magnetic susceptibilities of the complexes are shown in Table 2. Magnetic moments are of the magnitude expected for mononuclear nickel(I) complexes containing an unpaired electron.

I.r. Spectra

The i.r. spectra of all the complexes show the characteristic vibrations of the triphenylphosphine⁽⁵⁾ or triphenylarsine⁽⁵⁾ ligands. The weak absorption band located at 295 cm^{-1} in complex (1) can be assigned to the $\nu(\text{Ni-Cl})$ stretching vibration. This absorption is not observed in complex (4) probably because it is overlapped by a much more intense absorption due to an internal vibration of the ligand. Complex (7) shows an intense absorption at 335 cm^{-1} which must be assigned undoubtedly to the $\nu(\text{Ni-Cl})$ stretching vibration. Absorptions due to $\nu(\text{Ni-X})$, when $\text{X} = \text{Br}$ and I , must lie below 250 cm^{-1} as they are not observed in our spectra.

It is theoretically possible to postulate several square pyramidal or trigonal bipyramidal structures for the carbonyl complexes (7-9) but they all must show two $\nu(\text{C}\equiv\text{O})$ absorptions whichever be the symmetry group.

The three isolated complexes (7–9) show two absorption bands at 1996 and 1930 cm^{-1} which are independent of the nature of the halogen, so that it is not possible to distinguish between the various structures.

Experimental

Physical measurements

The i.r. spectra were recorded between 4000–250 cm^{-1} on a Perkin-Elmer spectrophotometer in KBr pellets. The room temperature magnetic susceptibilities were measured by the Gouy method using $\text{HgCo}(\text{SCN})_4$ as calibrant and by correcting for diamagnetism with the appropriate Pascal constants.

Analyses

C, H analyses were made with a Perkin-Elmer 240 micro-analyzer. Nickel was determined with dimethylglyoxime. Halogen was determined as described by White⁽⁶⁾.

Preparation of XNiL_3 complexes

An ethanolic (35 cm^3) solution of NaBH_4 (3 mmol) was added dropwise to an ethanolic solution (30 cm^3) containing the nickel(II) halide (6 mmol) and the ligand (18 mmol). The solution was stirred for 2h at room temperature and the crystalline precipitate formed was filtered and repeatedly washed with ethanol under nitrogen. Yield 50–60%.

The reactions with triethylphosphine, tributylphosphine and 1,2 bis-diphenylphosphineethane gave unchanged nickel(II) complexes, X_2NiL_2 .

Preparation of $\text{XNi}(\text{CO})_2\text{L}_2$ complexes

Carbon monoxide gas was bubbled through a suspension of each complex (1–3) in ethanol stirred at room temperature for 1h. The colour of the solid in suspension changes to give, finally, a crystalline precipitate which is filtered off and repeatedly washed with ethanol under nitrogen.

The reaction can be carried out also in benzene in which the initial complexes and the carbonyl derivatives formed are soluble. Partial evaporation of the benzene and the addition of hexane gives crystals of complexes (7–9).

The same reaction of complexes (4–6) in ethanol gives yellow crystalline precipitates which decompose rapidly in the solid on filtration, preserving their isolation. The reaction cannot be made in benzene as these carbonyl complexes decompose immediately in solution.

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