

Halonickel(I) Complexes

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Summary

The reduction of nickel(II) halides with NaBH_4 in the presence of different ligands, $\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3$, has been studied. With a molar ratio $\text{L}/\text{Ni} = 3$, new complexes $\text{NiX}(\text{SbPh}_3)_3$, $\text{X} = \text{Cl, Br, I}$, were obtained. With a molar ratio $\text{L}/\text{Ni} = 2$, dimeric species $[\text{NiXL}_2]_2$, $\text{X} = \text{Cl, Br, I}$; $\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3$, were isolated. They are unstable and decompose easily in the solid and rapidly in solution, so that pure samples were only identified for $\text{X} = \text{Cl, L} = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3$; $\text{X} = \text{Br, L} = \text{PPh}_3$ and $\text{X} = \text{I, L} = \text{PPh}_3$. With a molar ratio $\text{L}/\text{Ni} = 1$, complexes $[\text{NiXL}]_n$ (probably polymeric) were obtained. They are very unstable and pure samples could only be isolated when $\text{X} = \text{Cl, L} = \text{PPh}_3$. Impure substances containing variable amounts of decomposition products were obtained in all the remaining cases. The chemical and structural behaviour of these complexes is discussed.

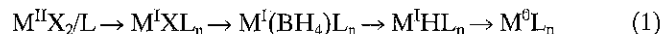
Introduction

The preparation of nickel(I) complexes of the type NiXL_3 , $\text{X} = \text{Cl, Br, I}$; $\text{L} = \text{PPh}_3^{(1-4)}, \text{AsPh}_3^{(4)}$ and NiXL_2 , $\text{X} = \text{Cl, Br, I}$; $\text{L} = \text{PCyclohexyl}^{(5)}$ and $\text{NiBr}(\text{PPh}_3)_2^{(6)}$ have been reported. More recently, various anionic and cationic^(7, 8) species have been described.

The chemical behaviour of complexes NiXL_3 is consistent whereas important divergencies are observed for complexes NiXL_2 in relation to their mono- or bi-nuclear structures and their tricoordinate, tetrahedral or square planar configurations. These differences moved us to complete our previous studies^(4, 7) on the reduction of nickel(II) salts with NaBH_4 in the presence of different ligand: Ni ratios of ligands $\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3$.

Results and Discussion

It has been established⁽⁹⁾ that the reduction of nickel(II) salts with NaBH_4 takes place through different intermediate complexes depending on the amount of the reducing agent, the time and the solvent, (see eq. (1));



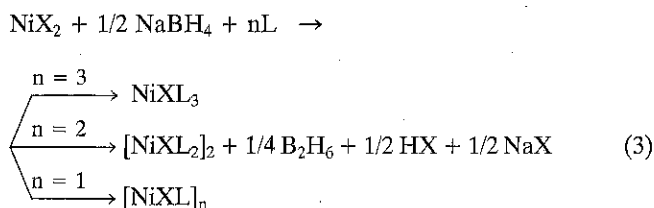
In order to isolate halonickel(I) complexes and prevent the occurrence of the following disproportionation reaction they must be insoluble in the solvent used



This explains why alkylphosphine and phosphite nickel(I) complexes which are soluble in ethanol could not be obtained. On the other hand, insoluble halonickel(I) complexes formed

in the first step of eq. (1) may be obtained in ethanol only if a small excess of the reducing agent is used, to assure the complete transformation of the starting compound, as the hydride or boranate simultaneously formed is completely soluble in ethanol.

In all the reactions, the strict stoichiometric amount of the reducing agent was used, as shown in eq. (3).



NiXL_3 complexes

The reduction of NiX_2 in the presence of SbPh_3 in a molar ratio 1:3 gives $\text{NiX}(\text{SbPh}_3)_3$ (where $\text{X} = \text{Cl, Br, I}$) as shown by the analytical data in Table 1. The chemical behaviour of these complexes is similar to that known for complexes of PPh_3 and $\text{AsPh}_3^{(4)}$, but they are less stable even in the solid state under nitrogen, and are very unstable in air and decompose in solution.

Magnetic measurements summarised in Table 2 are consistent with their formulation as Ni^{I} complexes (d^9). The calculated μ_{eff} are rather low, indicating a low orbital contribution which suggests an important tetragonal distortion of the tetrahedral environment⁽⁷⁾. The magnetic susceptibility variation between 195 and 300 K for $\text{NiCl}(\text{SbPh}_3)_3$ gives Weiss's constant $\theta = -15$ K. The distortion is also confirmed by the visible-u.v. spectra shown in Table 3. Thus, $\text{NiCl}(\text{PPh}_3)_3$ shows two absorption bands with maxima at 12500 and 10000 cm^{-1} assignable, respectively, to ${}^2\text{B}_2 \rightarrow {}^2\text{E}$ and ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$ transitions for a D_{2d} environment.

The assignments for the SbPh_3 complexes are less reliable, but asymmetric absorption bands located at 9800 ($\text{X} = \text{Br}$); 9500 ($\text{X} = \text{I}$) and 7240 ($\text{X} = \text{Br}$); 6850 ($\text{X} = \text{I}$) cm^{-1} may be attributed to the transitions described above. The chloro-complex could not be studied as it decomposed during the experiment in solution.

$[\text{NiXL}_2]_2$ complexes

The reactions shown in eq. (3) with $n = 2$ have been carried out for $\text{X} = \text{Cl, Br, I}$ and $\text{L} = \text{PPh}_3, \text{AsPh}_3$ and SbPh_3 . The resulting species are even less stable than NiXL_3 so that it is difficult to obtain pure samples. The disproportionation is more facile as the solubility is greater and therefore compounds with $\text{X} = \text{Br, I}$; $\text{L} = \text{AsPh}_3, \text{SbPh}_3$, could not be obtained as pure

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Table 1. Analytical data for the nickel(I) complexes.

Complex	Colour	Found (Calcd.)%			
		C	H	Ni	X
NiCl(SbPh ₃) ₃	brown	55.9(56.2)	3.8(3.9)	4.8(5.0)	3.0(3.0)
NiBr(SbPh ₃) ₃	pale red	53.8(54.1)	3.4(3.7)	4.7(4.9)	6.5(6.6)
NiI(SbPh ₃) ₃	dark red	52.0(52.1)	3.8(3.6)	4.8(4.7)	— (10.15)
[NiCl(PPh ₃) ₂] ₂	red	69.1(69.9)	5.0(4.9)	9.3(9.5)	5.7(5.7)
[NiCl(PPh ₃) ₂] ₂	yellow	70.4(69.8)	4.8(4.9)		
[NiCl(PPh ₃) ₂] ₂	orange	69.7(69.8)	5.1(4.9)		
[NiCl(AsPh ₃) ₂] ₂	red	61.5(61.2)	4.8(4.3)	7.8(8.3)	4.6(5.0)
[NiCl(SbPh ₃) ₂] ₂	red	53.6(54.0)	4.3(3.8)		
[NiBr(PPh ₃) ₂] ₂	red	66.2(65.2)	4.3(4.5)	8.6(8.8)	11.8(12.0)
[NiI(PPh ₃) ₂] ₂	brown	62.0(60.9)	4.5(4.3)		
[NiCl(PPh ₃) _n]	brown-red	60.9(60.6)	4.7(4.2)	15.8(16.4)	9.7(9.9)

Table 2. Magnetic data for the nickel(I) complexes.

Complex	T(K)	χ_M' (ucgs · mol ⁻¹ · 10 ⁻⁶)	μ_{eff} (BM)	θ (K)
NiCl(SbPh ₃) ₃	300	1810.9	2.06	-15.0
	195	2388.5	1.93	
NiBr(SbPh ₃) ₃	297	1566.6	1.93	
NiI(SbPh ₃) ₃	297	1205.4	1.71	
[NiCl(PPh ₃) ₂] ₂	293	1561.9	1.92	
[NiCl(PPh ₃) ₂] ₂ , red	197	2253.1	1.89	-16.3
[NiCl(PPh ₃) ₂] ₂ , yellow	296	1975.6	2.10	
[NiCl(AsPh ₃) ₂] ₂	296	1505.4	1.88	
[NiBr(PPh ₃) ₂] ₂	296	1828.8	2.07	
[NiCl(PPh ₃) _n]	293	1059.1	1.72	
	207	1613.0	1.64	-25.8

species. Complexes with X = Cl, L = PPh₃, AsPh₃, SbPh₃ and X = Br, I, L = PPh₃ were isolated as microcrystalline solids which have been formulated as NiXL₂ on the basis of the analytical data shown in Table 1.

NiCl(PPh₃)₂ may be chosen for discussion due to its relatively high stability. This complex is obtained as pale red crystals from ethanol. In benzene it gives an intense red solution, which becomes yellow-green after 10 min and eventually green after 20 min. The red colour may be maintained for longer periods by the addition of an excess of PPh₃. Evaporation of the red solution under vacuum gives yellow crystals after being washed with hexane. Occasionally they look orange.

The same compound can be obtained by adding a NaBH₄ solution in ethanol to a suspension of NiCl₂ in diethyl ether. The suspended solid dissolves completely to give a red solution from which orange crystals separate.

The yellow and the orange crystals as well as the microcrystalline solid obtained from ethanol have exactly the same analytical composition. We cannot find any reasonable explanation for these colour changes which produce only the differences observed in the electronic spectra.

The remaining compounds are not sufficiently stable to be handled under the same conditions and studies were carried out in the solid. The lack of stability precludes molecular weight measurements in solution. Even the most stable complex, NiCl(PPh₃)₂, gives too low a value (356) in 0.012 M benzene, due to decomposition, as can be directly observed. This contrasts with the Heimbach's proposal of the monomeric nature of the bromo-complex from cryoscopic determinations.

Magnetic measurements reveal that all the NiXL₂ complexes are paramagnetic with μ_{eff} corresponding to Ni^I(d⁹)

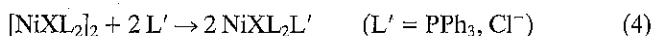
species. Weiss's constant $\theta = -16.3$ K was calculated for the chlorotriphenylphosphine complex measuring between 197 and 293 K.

Solution visible-u.v. spectra were recorded only for the most stable complexes and even they present absorption bands due to Ni^{II} impurities, increasing with time. All these complexes show one absorption band between 6000 and 6500 cm⁻¹ which is assigned to the T₂ → E transition in a T_d d⁹ configuration.

Both red and yellow forms of [NiCl(PPh₃)₂]₂ give the same spectrum in solution in benzene. Differences observed in the solid are not related to the tetrahedral geometry, common to both. This spectral behaviour, along with the other observations, suggests a dimeric halogen bridged structure. The existence of tricoordinate species in solution⁽¹⁾ proposed previously⁽⁶⁾ must be discarded. Reliable data have only been described for tricoordinate nickel tris(cyclohexyl)phosphine complexes⁽⁵⁾.

The i.r. spectrum of [NiCl₂(PPh₃)₂]₂ shows an absorption at 250 cm⁻¹ assignable to the ν (Ni-Cl) bridge stretching frequency. Bromo- and iodo-complexes do not show any absorption above 200 cm⁻¹ and the presence of more intense ligand absorptions prevents any discussion for the AsPh₃ and SbPh₃ derivatives.

In order to obtain additional information, some reactions with different ligands were performed



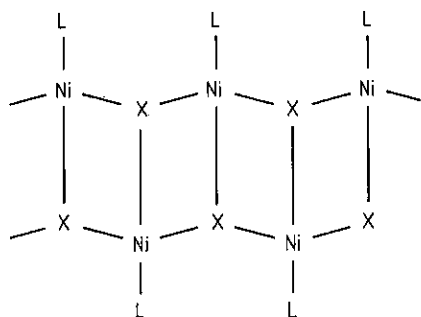
The use of these reactions is limited by the easy disproportionation of the starting complexes in solution. Otherwise, the reactions in suspension are too slow and frequently incomplete. The reaction with PPh₃ gave NiCl(PPh₃)₃⁽⁴⁾, and with [PPh₄]Cl gave [PPh₄][NiCl₂(PPh₃)₂]⁽⁷⁾.

[NiXL]_n complexes

The reduction when $n = 1$ (eq. (3)) gives solids which analyse as NiXL according to analytical data (Table 1). These compounds are less stable than those described above and only NiCl(PPh₃) was obtained pure.

A similar compound is obtained for X = Br but it always was impure. NiCl(PPh₃) is unaltered under nitrogen for several days. It is paramagnetic, with $\mu_{\text{eff}} = 1.72$ BM at room temperature, Weiss's constant being $\theta = -25.8$ K as measured between 207 and 293 K.

Benzene solutions of this complex show an absorption band at 6450 cm^{-1} which is assigned to the $T_2 \rightarrow E$ transition in a T_d environment, which, in agreement with μ_{eff} , may have an important tetragonal distortion. All these data may be rationalised by a structure such as



The i.r. spectrum shows an absorption which can be assigned to the metal-chlorine bridge stretching mode.

Reaction of NiCl(PPh₃) with 1 mol of PPh₃ in suspension in ethanol gives the dimer [NiCl(PPh₃)₂]₂ whereas the addition of an excess of the ligand gives the monomeric NiCl(PPh₃)₃. A similar rupture of the bridges can explain the solubility in polar solvents, with immediate decomposition.

Experimental

All the experiments were carried out under nitrogen and vacuum with the usual Schlenk-type glassware. Solvents were previously deoxygenated and dried (with the exception of EtOH which was the commercial absolute solvent). Commercial reagent grade nickel halides, NaBH₄, PPh₃, AsPh₃ and SbPh₃ were used without purification.

Elemental analyses were performed with a 240 B Perkin-Elmer microanalyser. Nickel was determined with dimethylglyoxime. Halogen was determined as described by White⁽¹⁰⁾. Molecular weights were measured with a Knauer vapour pressure osmometer.

Magnetic susceptibilities were determined by the Faraday method with a BE 15 Bruker balance between 200 K and room temperature.

Electronic absorption spectra were recorded in the solid by diffuse reflectance and in solution with a 330 Perkin-Elmer spectrophotometer. I.r. spectra were recorded in Nujol mulls or KBr pellets between $4000\text{--}200 \text{ cm}^{-1}$ in a 599 Perkin-Elmer spectrophotometer.

NiX(SbPh₃)₃

A solution of the hydrated nickel(II) halide (2.280 mmol) in EtOH was treated with SbPh₃ (2.420 g, 6.840 mmol). A solution of NaBH₄ (0.044 g, 1.160 mmol) recently prepared in EtOH was added dropwise to the stirred mixture at room temperature. After stirring for 30 min microcrystalline brown (1) (X = Cl), pale red (2) (X = Br) and dark red (3) (X = I) solids were obtained. Solids were repeatedly washed with EtOH and dried under vacuum. Yield ca. 70%.

*[NiCl(PPh₃)₂]₂**Method A*

A mixture of NiCl₂ · 6 H₂O (0.500 g, 2.100 mmol) and PPh₃ (1.100 g, 4.200 mmol) was stirred in EtOH (10 cm³). The dark green suspension was treated dropwise with a solution of NaBH₄ (0.040 g, 1.050 mmol) in the same solvent (20 cm³). The colour of the solid changed and after 30 min a microcrystalline red compound was isolated by filtration, washed with EtOH and hexane and dried under vacuum. Yield ca. 75%.

When this solid was dissolved in benzene and crystallized by evaporation, yellow crystals were obtained. Yield ca. 40%. However, if hexane is added to the benzene solution an orange crystalline solid results.

All these solids have exactly the same composition.

Method B

A suspension of NiCl₂ · 6 H₂O (0.250 g, 1.050 mmol) and PPh₃ (0.550 g, 2.100 mmol) was stirred in Et₂O (20 cm³) and treated dropwise with a solution of NaBH₄ (0.021 g, 0.550 mmol) in EtOH (10 cm³). The solid in suspension dissolved to give a clear red solution from which orange crystals separated. The compound was filtered, washed with EtOH and dried under vacuum. Yield ca. 60%. The analytical composition of this solid is exactly the same as those described above.

The following compounds, (5) (X = Cl, L = AsPh₃) brown; (6) (X = Cl, L = SbPh₃) red; (7) (X = Br, L = PPh₃) pale red; (8) (X = I, L = PPh₃) brown were prepared by method A, using the appropriate ligand.

Table 3. Electronic and i.r. spectra for the nickel(I) complexes.

Complex	Solid Diff. Refl. (cm ⁻¹)	Benzene Solution (cm ⁻¹)	Assignment	$\nu(\text{Ni-Cl})$ (cm ⁻¹)
NiBr(SbPh ₃) ₃	9800; 7240	—	${}^2B_2 \rightarrow {}^2A_1; {}^2B_2 \rightarrow {}^2E$	—
NiI(SbPh ₃) ₃	9520; 6850	—	${}^2B_2 \rightarrow {}^2A_1; {}^2B_2 \rightarrow {}^2E$	—
[NiCl(PPh ₃) ₂] ₂ red	—	6350	$T_2 \rightarrow E$	250
yellow	—	6350	$T_2 \rightarrow E$	250
[NiBr(PPh ₃) ₂] ₂	—	6060	$T_2 \rightarrow E$	—
[NiCl(PPh ₃) ₃] _n	—	6450	$T_2 \rightarrow E$	245

*Reactions of [NiCl(PPh₃)₂]₂**a) With PPh₃*

PPh₃ (0.220 g, 0.840 mmol) was added to a suspension of [NiCl(PPh₃)₂]₂ (0.520 g, 0.420 mmol) in EtOH (25 cm³) and the mixture was stirred for 2 h at room temperature. The colour of the suspended solid changed to red. The solid was filtered, washed repeatedly with EtOH and hexane and dried under vacuum. The solid was identified as NiCl(PPh₃)₃⁽⁴⁾.

A similar reaction was carried out with [NiBr(PPh₃)₂]₂ to give NiBr(PPh₃)₃⁽⁴⁾.

b) With [PPh₄]Cl

Under the same experimental conditions [NiCl(PPh₃)₂]₂ (0.700 g, 0.570 mmol) in EtOH (30 cm³) was treated with [PPh₄]Cl (0.390 g, 0.100 mmol) and stirred for 6 h at room temperature. The resultant microcrystalline solid, after filtration and repeated washing with EtOH and hexane, was identified as [PPh₄][NiCl₂(PPh₃)₂]⁽⁷⁾.

[NiCl(PPh₃)_n]

A solution of NaBH₄ (0.041 g, 1.080 mmol) in EtOH (20 cm³) was added dropwise to a mixture of NiCl₂ · 6H₂O (0.500 g, 2.100 mmol) and PPh₃ (0.550 g, 2.100 mmol). After the addition was complete the mixture was stirred for 30 min and the resulting microcrystalline dark brown-red solid was filtered, washed with EtOH and dried under vacuum. The analytical composition corresponded to the formulation [NiCl(PPh₃)_n]. Yield ca. 80%.

Similar reactions were performed for NiX₂ (X = Br, I) in the presence of PPh₃ and AsPh₃ and for NiCl₂ with AsPh₃; however, the resultant compounds were impure. The analyti-

cal composition was close to that required for the proposed formulation but the data were inconsistent.

Reaction of [NiCl(PPh₃)_n] with PPh₃

Using the experimental conditions described above for a similar reaction, [NiCl(PPh₃)_n] (0.370 g, 1.050 mmol) was treated with PPh₃ (0.270 g, 1.050 mmol) and the mixture was stirred for 4 h at room temperature. The resultant pale red solid was filtered, washed with hexane and dried under vacuum. This solid was identified as [NiCl(PPh₃)₂]₂.

The same reaction with an excess of PPh₃ gave a microcrystalline solid identified as NiCl(PPh₃)₃.

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Kinetics and Mechanism of Oxidation of *trans*-1,2-Diaminocyclohexanetetraacetatocobaltate(II) by Periodate

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Summary

The kinetics of oxidation of *trans*-1,2-diaminocyclohexanetetraacetatocobaltate(II), Co^{II}CDTA²⁻, by periodate were studied using either excess periodate or excess complex concentrations. When periodate was in excess the reaction showed first-order dependence on [IO₄⁻] and first-order and second-order dependences on [Co^{II}CDTA²⁻]. First-order dependence in each reactant was obtained when the complex was in excess. The reaction rate was found to be independent

of pH over the range 4–5, but increasing with increasing ionic strength. The enthalpy and the entropy of activation were calculated using the transition state theory equation.

Introduction

Periodate oxidations are believed to proceed *via* an inner-sphere mechanism. Its oxidations of organic substrates are specific when bridging groups, *e.g.* OH, NH₂, etc., are in the 1,2 positions with the formation of cyclic intermediates⁽¹⁾. An inner-sphere mechanism was proposed for iodide oxidation where an oxygen atom transfer with the formation of HOI as

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