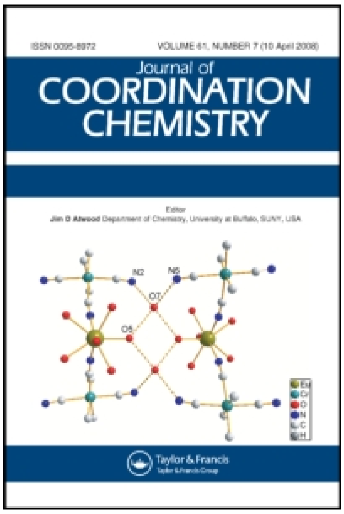

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# REACTIVITY OF ZEROVALENT NICKEL COMPLEXES. I. REACTIONS OF TETRAKIS(TRIETHYLPHOSPHITE)NICKEL(O) WITH MERCURY(II) HALIDES OR PSEUDOHALIDES

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The behaviour of $HgX_2$ (X = Cl, CN, NCS) towards $Ni[P(OEt)_3]_4$ has been studied. The reactions at room temperature in different solvents proceed readily, with formation of Ni(II) complexes and deposition of metallic mercury. $\{NiCl[P(OEt)_3]_4\}BPh_4$ and $Ni(CN)_2[P(OEt)_3]_3$ were respectively isolated from reactions with $HgCl_2$ and $Hg(CN)_2$. The reaction with $Hg(SCN)_2$ depends on the solvent; $Ni(NCS)_2$, $Ni(NCS)_2[P(OEt)_3]_2$ and $\{Ni[P(OEt)_3]_4\}(BPh_4)_2$ were isolated, respectively, from reactions in toluene, THF and ethanol. Only at -80°C does the reactoin with $Hg(SCN)_2$ take place without mercury deposition and a very unstable yellow solid, which is probably a bimetallic species, can be detected.

**Keywords:** Nickel, phosphites, halides, pseudohalides, complexes

## INTRODUCTION

Oxidative addition reactions of $HgX_2$ compounds (X = halide or pseudohalide) with zerovalent complexes of Pd and Pt have been described.[1] However, literature concerning about similar reactions with nickel compounds is scarce. Only the reactions of alkyl or aryl halides with Ni(O) complexes[2] and those of organomercuric compounds RHgX (R=Ph, X=Cl; $R=C_6F_5$, X=Br) with $Ni(PPh_3)_4$[3] have been reported.

Within a more general study on the reactivity of Ni(O) derivatives with $HgX_2$ compounds, we describe here the reactivity of $Ni[P(OEt)_3]_4$ towards $HgX_2$ (X=Cl, CN, NCS). The electronic and steric properties of $P(OEt)_3$ confers on $Ni[P(OEt)_3]_4$ a high stability. No appreciable dissociation of this complex in hexane and benzene solution is observed.[4]

## EXPERIMENTAL

All experiments were carried out under an argon atmosphere using standard Schlenck tube techniques and freshly distilled, dried and degassed solvents. Triethyl phosphite, Aldrich, was distilled before use. $Ni[P(OEt)_3]_4$ was prepared according to the literature method.[5] All other chemicals used were of reagent grade.

Elemental analyses were carried out by Elemental MicroAnalysis Ltd. Laboratories (Devon), England. Conductance measurements were made with a Phillips PW 9506 meter and a Phillips PW 9510/60 conductivity cell. Infrared spectra in the 4000-200 $cm^{-1}$ range were recorded on a Perkin-Elmer 325 spectrophotometer. Electronic spectra were obtained using a UVIKON 620 spectrophotometer. The diffuse reflectance spectra were measured on the same spectrophotometer with the standard

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Kontron diffuse reflectance accessory and $BaSO_4$ as diluent and reference. Proton NMR spectra were recorded on a Varian T-60-A with tetramethylsilane as internal standard.

*Reaction with* $Hg(CN)_2$ *in THF*

To a solution of $Ni[P(OEt)_3]_4$ (0.1g, 0.14 mmol) in THF (10 $cm^3$) was added solid $Hg(CN)_2$ (0.035 g, 0.14 mmol) with stirring. A grey powder of metallic mercury was formed; the solution was orange in colour. After several hours the solution was filtered and concentrated under vacuum to remove all solvent. An orange oil formed from which all attempts to obtain a solid were fruitless. However, the i.r. and electronic spectra of the oil correspond to those of $Ni(CN)_2[P(OEt)_3]^3$ as previously described.[6]

*Reaction with* $Hg(SCN)_2$ *in THF*

To a solution of $Ni[P(OEt)_3]_4$ (0.1g, 0.14 mmol) in THF (10$cm^3$) was added solid $Hg(SCN)_2$ (0.043 g, 0.14 mmol) with stirring. The solution was red in colour. From the green solution resulting from stirring and filtration of the metallic mercury formed, a green powder, $Ni(NCS)_2[P(OEt)_3]_2$ precipitated after concentration under vacuum and addition of petroleum ether. (Found: C, 31.98, H, 5.61; N, 5.78%. $C_{14}H_{30}N_2NiO_6P_2S_2$ requires C, 33.15, H, 5.96; N, 5.52%).

*Reaction with* $Hg(SCN)_2$ *in EtOH*

To a solution of Ni $P(OEt)_3$ $_4$ (0.1g; 0.14mmol) in EtOH (10 $cm^3$) was added solid $Hg(SCN)_2$ (0.043g, 0.14 mmol) with stirring. To the dark red solution resulting, after separation of the metallic mercury formed, a solution of $NaBPh_4$ in ethanol was added. By cooling, a yellow powder, $\{Ni[P(OEt)_3]_4\}(BPh_4)_2$, precipitated, m.p. 92°C (Found:C, 63.41; H, 7.19%; $B_2C_{72}H_{100}NiO_{12}P_4$ requires C, 63.48; H, 7.34%). $\Phi_\infty = 144.57^{-1}$ $cm^2$ $mol^{-1}$ in acetone.

*Reaction with* $Hg(SCN)_2$ *in toluene*

The reaction carried out under similar conditions in toluene (10 $cm^3$) yielded, after 6 days of stirring at room-temperature, a yellow powder identified as $Ni(SCN)_2$.

*Reaction with* $HgCl_2$ *in EtOH*

To a solution of $Ni[P(OEt)_3]_4$ (0.1 g; 0.14 mmol) in ethanol (10 $cm^3$) was added solid $HgCl_2$(0.037 g, 0.14 mmol) with stirring. After separation of the metallic mercury formed a solution of $NaBPh_4$ in ethanol was added to the dark red solution and the reaction mixture was heated. With subsequent cooling a dark red crystalline solid, $\{Ni[P(OEt)_3]_4Cl\}BPh_4$, formed, m.p. 94-96°C (Found: C, 55.21; H, 7.34%. $BC_{48}ClH_{80}NiO_{12}P_4$ requires C, 53.45; H, 7.42%); $\Lambda_\infty = 83.47^{-1}$ $cm^2$ $mol^{-1}$ in acetone. $\delta_H[(CD_3)_2CO]$ 7.2-6.5 3(20H, m, $BPh_4$), 4.26-3.95 (24H, m, $12CH_2$), 1.27 (36H, t, J 7$H_z$, $12CH_3$).

*Reaction of* $NiCl_2\cdot 6H_2O$ *with* $P(OEt)_3$ *in EtOH*

To a solution of $NiCl_2\cdot 6H_2O$ (0.14 mmol) in ethanol (10 $cm^3$) was added an excess of $P(OEt)_3$ with stirring. To the resulting dark red solution a solution of $NaBPh_4$ in ethanol was added and the reaction mixture was heated. With cooling a dark red crystalline solid was formed, and this was identified as $\{Ni[P(OEt)_3]_4Cl\}BPh_4$.

When the dark red solution was stirred for 24 h and heated after addition of a solution of $NaBPh_4$ in ethanol, a yellow solid formed and was identified as $\{Ni[P(OEt)_3]_4\}(BPh_4)_2$.

### *Reaction of Ni(NCS)$_2$ with P(OEt)$_3$ in EtOH*

To a suspension of Ni(NCS)$_2$ (0.14 mmol) in ethanol (10 cm$^3$), was added an excess of P(OEt)$_3$ with stirring. A dark red solution formed. All attempts to obtain a solid were fruitless. The i.r. and electronic spectra of the solution are consistent with a formulation of the type {Ni[P(OEt)$_3$]$_5$} (NCS)$_2$.

## RESULTS AND DISCUSSION

The reactions of tetrakis(triethylphosphite)nickel-(O) with halides or pseudohalides of mercury proceed readily at room temperature in different solvents with liberation of mercury and formation of Ni(II) compounds. An oxidation of Ni(O) by Hg(II) takes place in each case. The nature of the Ni(II) compounds formed depends on the HgX$_2$ salt used and the solvent. Scheme 1 summarizes the reactions observed at room temperature.

The oxidation of Ni(O) to Ni(II) probably proceeds through a heterobimetallic compound analogous to that formed in the reaction of Ni(PPh$_3$)$_4$ with (C$_6$F$_5$)$_2$Hg[3]. We have observed the formation of a yellow solid without separation of mercury metal in the reaction with Hg(SCN)$_2$ in ethanol at -80°C, which decomposes at higher temperatures and is probably a bimetallic intermediate.

Table I gives the principal i.r. frequencies and the electronic spectral data for the new compounds obtained. The $\nu$(P = O) bands are displaced in all compounds with respect to the free ligand. The conductance values obtained for freshly prepared solutions of {Ni[P(OEt)$_3$]$_4$Cl}(BPh$_4$)$_2$ correspond to 2:1 and 1:1 electrolytes, respectively, containing bulky ions. In both cases the i.r. and $^1$H NMR spectral data are consistent with the presence of free BPh$_4^-$ ion. A square planar configuration for {Ni[P(OEt)$_3$]$_4$}(BPh$_4$)$_2$ is deduced from the electronic spectrum of the solid.[7] However, in solution, an interaction

Scheme 1

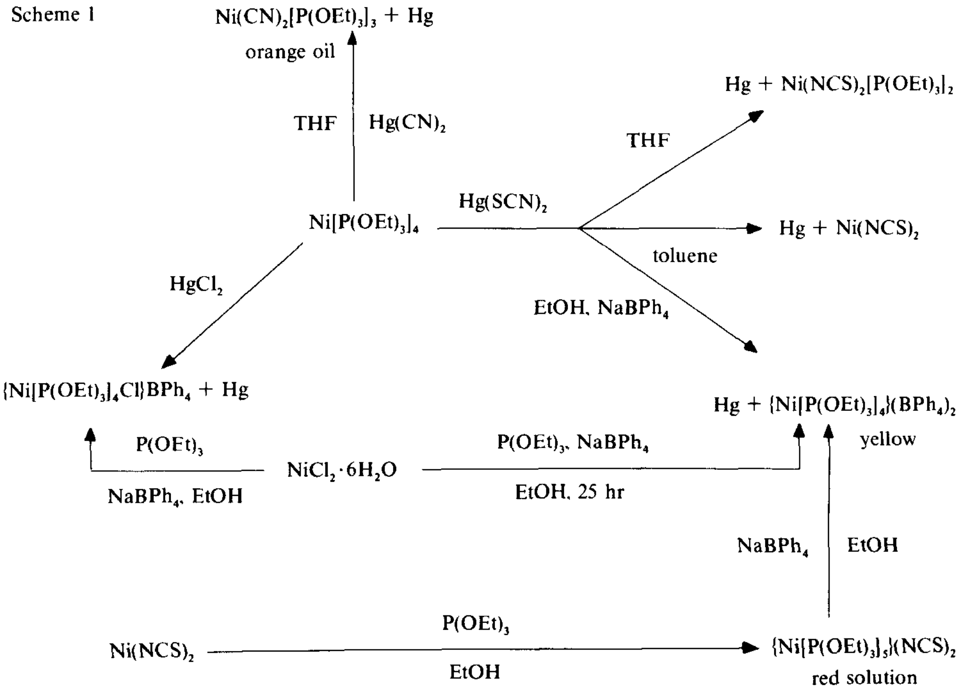

TABLE I
Characteristic data for the Ni complexes

| Compound | Colour | I.R. data[a] (cm$^{-1}$) | | Electronic spectra data λ(cm$^{-1}$), ε[b] | Solvent |
|---|---|---|---|---|---|
| $Ni(CN)_2[P(OEt)_3]_3$ | orange | 2118 s | ν(CN) | 29,411; 24,390 sh | solid |
| $Ni(NCS)_2[P(OEt)_3]_2$ | green | 2120 vs | ν(CN) | 24,390; 15,151; 13,888 sh | solid |
| | | | | 24,400(10); 14,859(4); 13,333(3) | THF |
| $\{Ni[P(OEt)_3]_4\}(BPh_4)_2$ | yellow | 1230, s, br | ν(P=O) | 23,256 | solid |
| $\{Ni[P(OEt)_3]_4Cl\}BPh_4$ | red | 1240, s, br | ν(P=O) | 23,810; 18,182 | solid |
| | | | | 23,840(575); 18,220 sh (91) | acetone |
| $\{Ni[P(OEt)_3]_5\}(NCS)_2$ | red | $2080^{c}_{s}$ | ν(CN) | 24,390(1190); 20,000 sh (674) | EtOH |

[a] In nujol; [b] values of ε in M$^{-1}$ cm$^{-1}$; [c] in EtOH solution.

with the solvent takes place and $^1H$ NMR spectrum indicates the presence of paramagnetic species.

The absorptions observed in the electronic spectrum of $\{Ni[P(OEt)_3]_4Cl\}BPh_4$ in the solid state and dissolved in acetone correspond to a five-coordinate species.[8] In the i.r. spectrum a ν(Ni-Cl) absorption at 330 cm$^{-1}$ is observed. The green compound $Ni(NCS)_2[P(OEt)_3]_2$ shows a ν(C=N) band at 2120 cm$^{-1}$ in the range reported for $Ni(NCS)_2(ROH)_2$,[9] for which a distorted octahedral environment with bridging thiocyanate ligands was proposed. The electronic spectrum of $Ni(NCS)_2[P(OEt)_3]_2$ in THF shows absorption maxima at 24400, 14859 and 13333 cm$^{-1}$, which can be assigned to Ni(II) ions in an octahedral environment on the basis of similarity with the electronic spectrum of $Ni(NCS)_2(MeOH)_2$.[9] Under either pressure or vacuum this compound loses $P(OEt)_3$ and $Ni(NCS)_2$ is formed. It is to be noted that the ethanolic solutions from which $\{Ni[P(OEt)_3]_4Cl\}(BPh_4)$ is isolated by addition of $NaBPh_4$ become green in colour after several hours, but from these solutions crystalline solids could not be isolated.

In the reactions of $Ni[P(OEt)_3]_4$ with $Hg(SCN)_2$ the deposition of free mercury was accompanied by the formation of a red species in solution. The i.r. and electronic spectral data of these solutions are identical with those of $Ni(NCS)_2$ in ethanol or benzene in the presence of an excess of $P(OEt)_3$. The spectral and magnetic data for this species were attributed to the square planar complex $\{Ni[P(OEt)_3]_4\}(SCN)_2$.[7] In attempts to isolate these red square planar species only a yellow solid, identical with that obtained in the reaction of $Ni[P(OEt)_3]_4$ with $Hg(SCN)_2$, was obtained. However, the red complex present in solution is probably the five-coordinate species $\{Ni[P(OEt)_3]_5\}(NCS)_2$. The electronic spectrum of this solution shows a lower energy absorption maximum at 24390 cm$^{-1}$ with a shoulder at 20,000 cm$^{-1}$ which can be assigned to a $\nu_1$ $(e'')^4(e')^3(a_1)^1 \longleftarrow (e'')^4(e')^4$ transition split for a $D_{3h}$ symmetry. Similar absorptions have been described for $\{Ni[P(OEt)_3]_5\}(ClO_4)_2$ in the solid state and in solution in the presence of an excess of ligand. In solution the equilibrium $NiL_5^{2+} \rightleftharpoons NiL_4^{2+} + L$ can account the observed spectral data.[10]

In the reaction of $Ni[P(OEt)_3]_4$ with $Hg(CN)_2$ the deposition of free mercury was accompanied by the formation of an orange oil identified by i.r. and electronic spectra[9] as $Ni(CN)_2[P(OEt)_3]_3$.

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