

## SYNTHESIS AND REACTIVITY OF NICKEL *o*-SEMIQUINOLATE COMPLEXES

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### Summary

The hindered catecholate complex  $K_2Ni(\text{C}_6\text{H}_2(\text{t-Bu})_2\text{O}_2)_2$  was obtained by the reaction of nickel halides with the dipotassium derivative of 3,5-di-*t*-butylcatechol. The oxidation of this complex leads to a compound with a semiquinolate structure:

$Ni(\text{C}_6\text{H}_2(\text{t-Bu})_2\text{O}_2)_2$  ( $\text{C}_6\text{H}_2(\text{t-Bu})_2\text{O}_2 = \text{sq}$ ) which is identical to the previously

prepared Balch complex. Reactions of bis(3,5-di-*t*-butyl-1,2-benzo-semiquinolate)-nickel with acids, alkali, benzoyl peroxide and some complex molecular compounds were investigated. The reduction of  $Ni(\text{SQ})_2$  with BuLi in the presence of donor ligands can be a convenient method of synthesising nickel zerovalent complexes. Tetrakis(triphenylphosphine)nickel prepared by this procedure undergoes oxidative addition reactions with allyl chloride and benzoyl peroxide. The mono-*o*-semiquinolate nickel derivative allylnickel-3,5-di-*t*-butyl-1,2-benzo-semiquinolate was produced. This novel allylnickel complex is air-stable and paramagnetic both in solution and in the solid state.

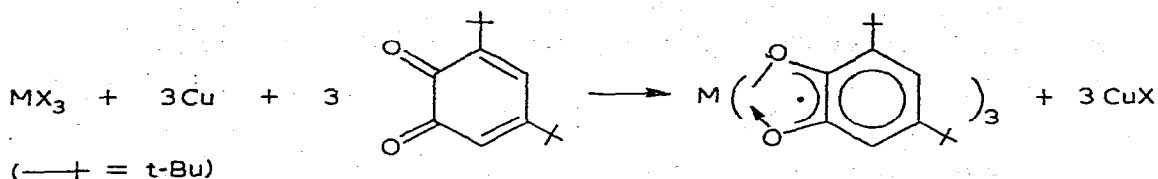
### Introduction

There are comparatively few publications in the literature dealing with transition metal complexes with *o*-quinone fragments [1–4]. Pierpont and coworkers have reported the preparation of tris ligand complexes of Cr, Mo and W by the interaction of *o*-chloranil with hexacarbonyls of these elements, Analogously Balch has synthesized the diligand nickel complex by the reaction of tetracarbonylnickel with 3,5-di-*t*-butyl-1,2-benzoquinone. On the basis of its complex paramagnetic properties and poor solubility the author has suggested a polymeric structure with an octahedral coordinative nickel atom.

Recently we have published a number of papers [5–8] concerning transition metal complexes (Cu, Ag, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, La, Gd, Pd) with

*o*-quinone fragments. Apart from the derivatives of Cu, Ag and Pd these compounds comprise the tris ligand complexes, in which the ligand has the structure of the *o*-semiquinolate anion radical [5,6] or catecholate dianion [6]. The above-mentioned tris ligand derivatives can be synthesized by the following methods.

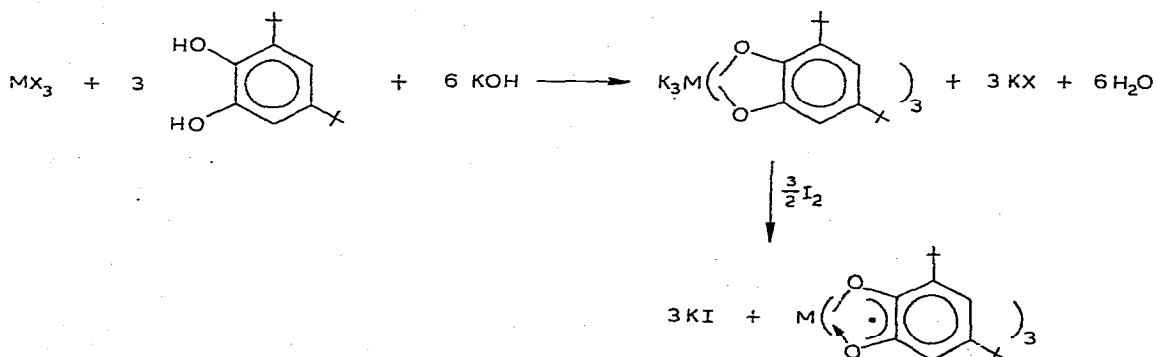
(1) Interaction of metal halides and *o*-quinones in the presence of metallic copper



(2) Reaction of transition metal halides with *o*-semiquinolates of sodium and thallium

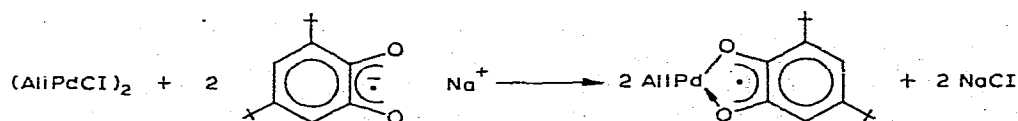
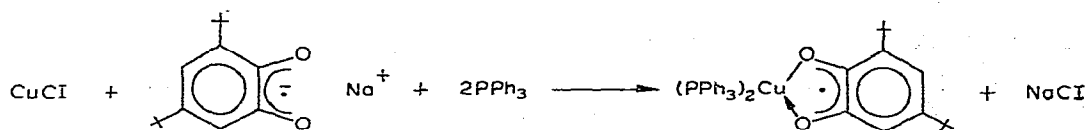


(3) Exchange reaction of transition metal salts with the dianion of 3,5-di-*t*-butylcatechol



Tris-*o*-semiquinolate complexes of transition metals are rather stable in the solid state in air, and readily soluble in all organic solvents.

Mono-*o*-semiquinolate complexes of Cu, Ag and Pd containing a neutral donor ligand or a  $\pi$ -allyl group can be prepared by the following methods

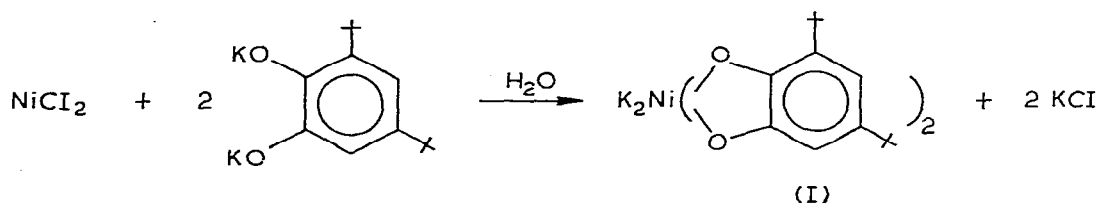


AlI =  $\pi$ -C<sub>3</sub>H<sub>5</sub>

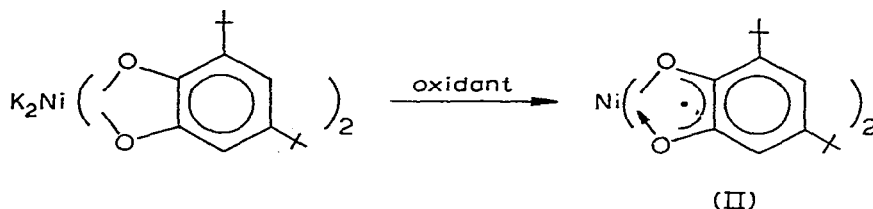
In this paper we report the synthesis and reactivity of nickel *o*-semiquinolate derivatives.

## Results and discussion

The pale yellow crystalline compound I was prepared by the reaction of nickel chloride with the dipotassium derivative of 3,5-di-*t*-butylcatechol in the absence of oxygen. I is insoluble in water and hydrocarbons, but moderately soluble in diethyl ether. The preparation is very sensitive to air and other oxidants. Comparison studies of such reactions for Group V and VI transition metals, Fe group and lanthanides [6] suggest that compound I has a catecholate structure

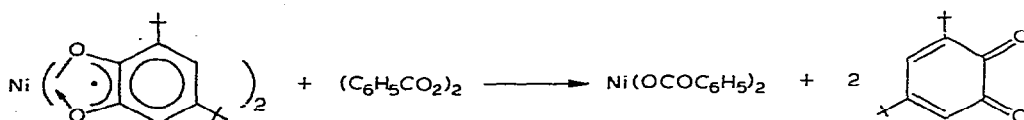


The latter oxidation leads to another derivative, II, being identical in composition to the Balch complex [4]



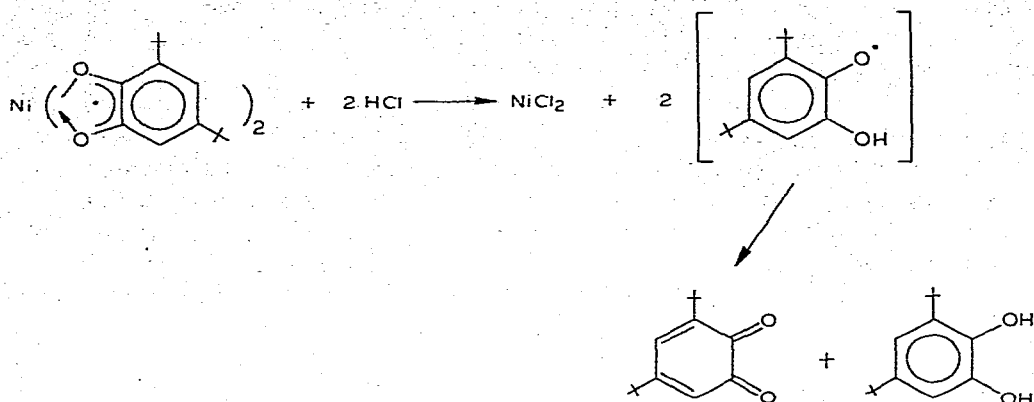
Ni(SQ)<sub>2</sub> is a greenish-brown substance, airstable in the solid state, but in solution, especially in polar medium, it quickly decomposes with quinone liberation. Unlike the Balch complex (II) it is readily soluble in all organic solvents. The cryoscopic determination of the molecular weight showed Ni(SQ)<sub>2</sub> to be monomeric in solution. According to the magnetic susceptibility data there are two unpaired electrons in the molecule of the complex,  $\mu_{\text{ef}} = 2.90 \mu_{\text{B}}$ , being independent of temperature. A series of experimental facts (the absence of stretching frequencies of the quinone CO group, the easy cleavage of the nickel–ligand bond by alcohol/tetrahydrofuran solution [9]) together with literature analysis data allows us to treat this diligand complex as a derivative with two *o*-semiquinolate anion radicals.

Bis(3,5-di-*t*-butylbenzosemiquinolate-1,2)nickel is a very reactive compound. At room temperature in toluene solution, complex II quantitatively reacts with benzoyl peroxide to give nickel dibenzoate and 3,5-di-*t*-butylbenzoquinone-1,2:



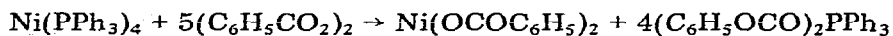
The reaction of II and gaseous HCl when carried out in toluene with starting

reagents in the ratio 1 : 2 leads to ligand substitution:



Nickel hydroxide and dipotassium 3,5-di-*t*-butylcatecholate are formed by treatment of II with alcohol alkali in excess.

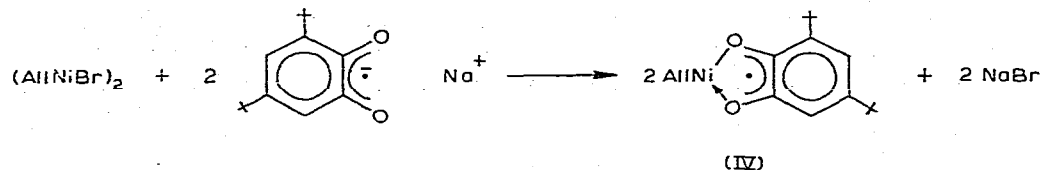
The reaction of bis(*o*-semiquinolate)nickel complex with triphenylphosphine in the presence of butyllithium in excess is of considerable interest. The red-brown crystalline product formed was the zerovalent nickel complex  $\text{Ni}(\text{PPh}_3)_4$  (III). This is confirmed by its analytical data and chemical behaviour. III is readily soluble in toluene, slightly soluble in diethyl ether and quickly oxidizes in air. Tetrakis(triphenylphosphine)nickel is readily involved in zerovalent complex characteristic reactions of oxidative addition. The interaction of III and benzoyl peroxide produces nickel dibenzoate and triphenylphosphine dibenzoate



The reaction between  $\text{Ni}(\text{PPh}_3)_4$  and allyl chloride gives the dark red crystalline compound  $\text{AlNiCl} \cdot 2 \text{PPh}_3$  (m.p. 89–92°C), being stable in air over short periods.

Thus, from our viewpoint, the reaction of bis(3,5-di-*t*-butylbenzosemiquinolate-1,2)nickel with donor ligands is suitable for zerovalent nickel complex synthesis.

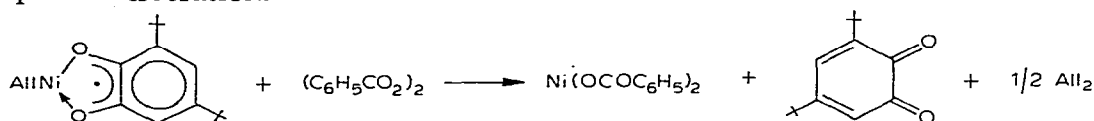
Besides the diligand nickel complex we have synthesized the mono-*o*-semiquinolate derivative allylnickel-3,5-di-*t*-butylbenzosemiquinolate-1,2. The latter compound was obtained in the same manner as the corresponding palladium complex [7].



IV is a dark green substance with melting point 165–168°C which is soluble in ordinary organic solvents and is monomeric in solution. It should be noted that this novel nickel complex is air-stable in the solid state, but is readily oxidized

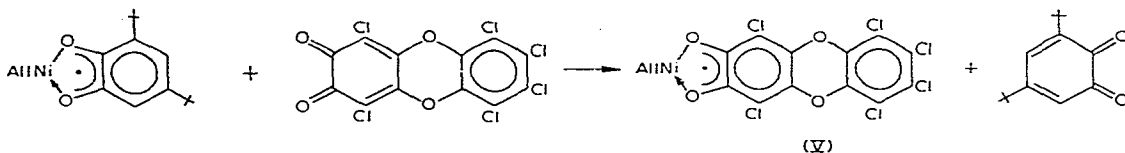
in solution. Allylnickel-3,5-di-*t*-butylbenzosemiquinolate-1,2 is paramagnetic both in solution and in the solid state. The ESR spectrum parameters of IV in solution ( $g = 2.0032$ ,  $a_H = 3.2 G$ ) are essentially the same as for alkali metal *o*-semiquinolates [10], which confirms unpaired electron localization on the *o*-semiquinonic fragment. Consequently, allylnickel-3,5-di-*t*-butylbenzosemiquinolate-1,2 represents a complex with free-radical ligand. The individual components of the ESR spectrum are rather broad to resolve the additional HFS, resulting from the magnetic isotope  $^{61}\text{Ni}$ , (natural abundance of about 1.19%,  $J = 3/2$ ,  $\mu = -0.7487$ ).

It should be noted that there are some differences in the chemical behaviour of allylnickel-3,5-di-*t*-butylbenzosemiquinolate-1,2 and its palladium analogue. Thus, unlike allylpalladium 3,5-di-*t*-butylbenzosemiquinolate-1,2 [7] no exchange reactions were observed between IV and donor ligands (triphenylphosphine, *o*-phenanthroline) with allyl radical liberation. The interaction of IV as well as the bis(*o*-semiquinolate)nickel complex (II) with benzoyl peroxide leads to quinone liberation.

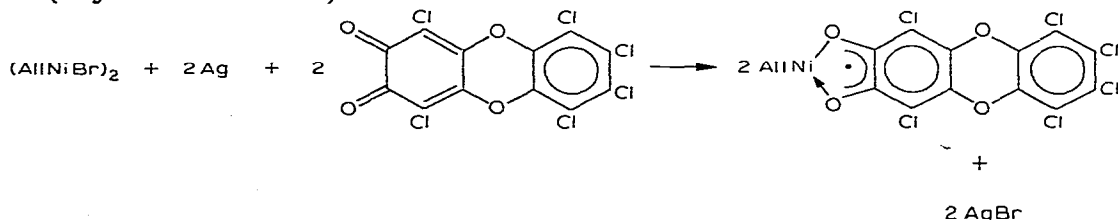


It is of interest that under the same conditions the reaction of the analogous palladium compound and benzoyl peroxide yields metallic palladium.

Just as with other *o*-semiquinolate metal complexes [8], the 3,5-di-*t*-butylbenzosemiquinolate-1,2 fragment can be substituted by other *o*-semiquinonic ligands with greater oxidative potential



The formation of V can be easily registered by electron spin resonance. The ESR signal represents a singlet with satellites due to splitting on isotope  $\text{Ni}^{61}$  ( $g = 2.0047$ ,  $a_{\text{Ni}^{61}} = 5.1 G$ ). The other method of preparation of V is the reduction of perchloroanthrenequinone-2,3 by metallic silver in the presence of bis(allylnickel bromide).



## Experimental

### Bis(3,5-di-*t*-butylbenzosemiquinolate-1,2)nickel (II)

A solution of 1.3 g (0.01 mol)  $\text{NiCl}_2$  in 30 ml  $\text{H}_2\text{O}$  was added under argon to a solution of dipotassium 3,5-di-*t*-butylcatecholate in 40 ml  $\text{H}_2\text{O}$ , prepared from

4.44 g (0.02 mol) of 3,5-di-*t*-butylcatechol [11] and 2.24 g (0.04 mol) KOH to

precipitate pale yellow  $\text{K}_2\text{Ni}(\text{C}_{28}\text{H}_{40}\text{O}_4)_2$  (I). After oxidation of I greenish-brown

II is formed, which is extracted with hexane several times. Yield 80%. Anal. Found: C, 66.62; H, 8.16; Ni, 11.52.  $\text{C}_{28}\text{H}_{40}\text{O}_4\text{Ni}$  calcd.: C, 67.33; H, 8.02; Ni, 11.82%. Mol. wt.: found, 546; calcd., 499.

#### *Tetrakis(triphenylphosphine)nickel*

A solution of 0.5 mol BuLi in pentane under inert atmosphere was added to a mixture of bis(3,5-di-*t*-butylbenzosemiquinolone-1,2)nickel (2.5 g, 0.05 mol) and  $\text{PPh}_3$  (5.24 g, 0.2 mol) in 50 ml toluene at room temperature to give a stable dark red colour to the solution. The red-brown product formed was filtered off and washed with ether and dried in vacuo to give crystalline  $(\text{PPh}_3)_4\text{Ni}$ . Melting point, 120–123°C. Anal. Found: C, 76.95; H, 5.23.  $\text{C}_{72}\text{H}_{60}\text{P}_4\text{Ni}$  calcd.: C, 77.70; H, 5.40; Ni, 5.30; P, 11.60%.

#### *Bis(triphenylphosphine)allylnickel chloride*

To a solution of  $\text{Ni}(\text{PPh}_3)_4$  in ether was added an ether solution of allyl chloride. The mixture became colourless and dark red crystals were precipitated. After removal of  $\text{PPh}_3$  and recrystallization,  $\text{AllylNiCl} \cdot 2 \text{PPh}_3$  has m.p. 89–92°C. Anal. Found: C, 70.42; H, 5.80; Cl, 4.86.  $\text{C}_{39}\text{H}_{35}\text{ClP}_2\text{Ni}$  calcd.: C, 70.96; H, 5.31; Cl, 5.38%.

#### *Allylnickel 3,5-di-*t*-butylbenzosemiquinolone-1,2 (IV)*

To a solution of  $(\text{AllylNiBr})_2$  [12] (1.64 g, 9 mmol) in 50 ml ether was added under inert atmosphere 30 ml ether solution of sodium 3,5-di-*t*-butylbenzosemiquinolone (obtained by treating 4.5 mmol 3,5-di-*t*-butylbenzoquinone-1,2 [11] with 4.5 mmol disodium derivative of 3,5-di-*t*-butylcatechol). The initial red colour of the solution changed to green. Ether was removed under reduced pressure. The dark residue was treated with hexane several times. After evaporation of hexane a dark green compound was produced with m.p. 165–168°C. Anal. Found: C, 63.53; H, 8.01; Ni, 18.05.  $\text{C}_{17}\text{H}_{25}\text{O}_2\text{Ni}$  calcd.: C, 63.75; H, 7.81; Ni, 18.44%. Mol. wt.: found, 328; calcd., 320.

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