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## NEW NICKEL(II), PALLADIUM(II) AND PALLADIUM(0) DERIVATIVES OF *p*-DIETHYNYLBENZENE

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### Summary

Reaction of  $\text{Ni}(\text{NCS})_2(\text{NH}_3)_4$  and  $[\text{Pd}(\text{CN})_2\text{en}]$  with the dipotassium salt of *p*-diethynylbenzene in liquid ammonia has given the homoleptic complexes  $\text{K}_2[\text{M}(\text{p-PDE})_2]$  ( $\text{M} = \text{Ni}, \text{Pd}$ ) ( $\text{p-PDE} = \text{p}-(\text{C}\equiv\text{C})_2\text{C}_6\text{H}_4$ ). Reduction of the  $\text{Pd}^{\text{II}}$  complex with potassium in the same solvent gave the complex  $\text{K}_4[\text{Pd}(\text{p-PDE})_2]$ . These diamagnetic and polymeric complexes are very unstable to oxidation and hydrolysis. The reaction of the same dipotassium salt with  $\text{MX}_2(\text{Ph}_3\text{P})_2$  complexes ( $\text{M} = \text{Ni}, \text{Pd}$ ;  $\text{X} = \text{halide}$ ) gave a new type of heteroleptic palladium(II) derivatives  $\text{K}_2[\text{Pd}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C})_2(\text{Ph}_3\text{P})_2]$ , but it was not possible to isolate the corresponding heteroleptic compound of  $\text{Ni}^{\text{II}}$ . The observations are discussed in terms of a proposed mechanism for the reactions.

### Introduction

In recent years a large variety of organometallic compounds containing alkynyl ligands attached to Ni, Pd or Pt have been described. Most of these are neutral heteroleptic compounds with phosphine or arsine ligands and monoalkynyl groups. A few examples of homoleptic alkynyl compounds are also known [1].

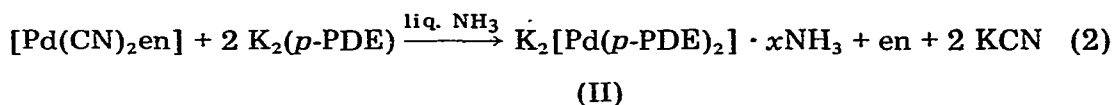
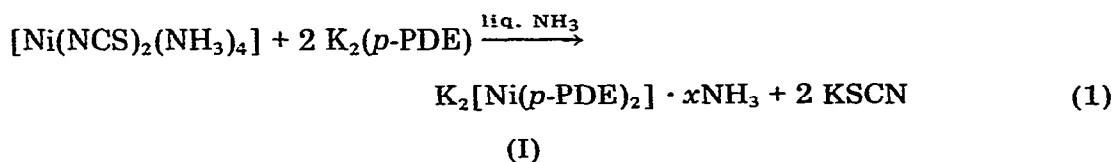
It was our objective to synthesise new homoleptic and heteroleptic derivatives of Ni and Pd containing the bifunctional ligand *p*-phenylenediethynylide (*p*-PDE) using liquid ammonia as solvent. The heteroleptic  $\text{H}_2(\text{p-PDE})$ -derivatives  $\text{Pd}^{\text{II}}$  and  $\text{Pt}^{\text{II}}$  of the type *trans*- $[(\text{R}_3\text{P})_2\text{XM}-\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C}-\text{MX}(\text{PR}_3)_2]$  and *trans*- $[(\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{C})_2\text{M}(\text{PR}_3)_2]$ , in which the bis-alkyne acts as a bridged or monofunctional ligand, respectively, have been described [2–4]. However, only one heteroleptic  $\text{Ni}^{\text{II}}$  derivative *trans*- $[\text{Ni}(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_2(\text{Ph}_3\text{P})_2]$  is known [5].

In an attempt to explain the different modes of reaction of the Ni and Pd  $\text{MX}_2(\text{Ph}_3\text{P})_2$  complexes we propose a mechanism for the reactions of the Ni complexes with alkali acetylides in liquid ammonia which takes account of the different ammonolysis behaviour observed for these complexes [6].

## Results and discussion

### Preparation of homoleptic derivatives

Nickel(II) and palladium(II) homoleptic derivatives have been prepared from the ammonia-soluble complexes  $\text{K}_2[\text{Ni}(\text{CN})_4]$ ,  $[\text{Ni}(\text{NCS})_2(\text{NH}_3)_4]$ ,  $[\text{Ni}(\text{NH}_3)_6]\text{I}_2$ ,  $\text{Pd}(\text{CN})_2$  and  $[\text{Pd}(\text{CN})_2\text{en}]$ . The reactions of all these complexes with dipotassium *p*-phenylenediethynylide in liquid ammonia led to a complete replacement of the ligands by alkynyl groups, independent of the molar ratio of reactants, as indicated by the eqs. 1 and 2.



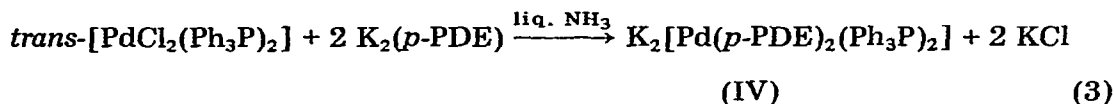
The nickel derivative is a crystalline solid, deep yellow in colour, whereas the palladium derivative is a lamellar solid, light ochre in colour. Both solids contain a variable amount of  $\text{NH}_3$ , which can be partly removed under high vacuum.

Reaction of a solution of II in liquid ammonia with a solution of potassium in the same solvent gave a microcrystalline compound (III), yellow-orange in colour. Its stability to oxidation and hydrolysis is considerably lower than that of II. For example, III reacts explosively with water or air, and so cannot be satisfactorily analysed. This product is probably the  $\text{Pd}^0$  compound  $\text{K}_4[\text{Pd}(p\text{-PDE})_2]$ . The presence of empty  $\pi^*$  orbitals in the alkynyl ligand makes possible the formation of metal derivatives in low oxidation states. Its stability to oxidation is very low, as expected from the low  $\pi$ -acceptor capacity of the alkynyl compared with the carbonyl ligands. The very unstable  $\text{Pd}^0$  complex  $\text{K}_4[\text{Pd}(\text{CN})_4]$  [7] is known, but no  $\text{Pd}^0$  complexes with bifunctional alkynyl ligands have been previously reported.

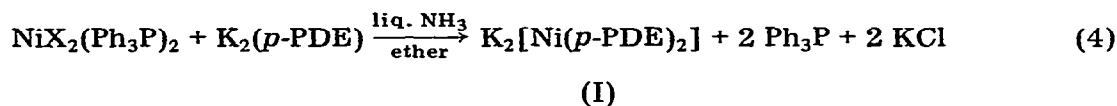
### Preparation of heteroleptic derivatives

Numerous heteroleptic derivatives of the type  $[\text{M}(\text{C}\equiv\text{CR})_2(\text{R}'_3\text{P})_2]$  ( $\text{R}, \text{R}' = \text{alkyl, aryl}$ ) have been described, the first of them being obtained by Chatt and Shaw [8] by reaction of  $\text{MX}_2(\text{R}'_3\text{P})_2$  complexes with an alkali metal salt of the alkyne in liquid ammonia/ether ( $\text{M} = \text{Ni}$ ) or liquid ammonia ( $\text{M} = \text{Pt}$ ). Other preparative routes have been more recently described [9] which were used principally for  $\text{Pd}^{\text{II}}$  and  $\text{Pt}^{\text{II}}$  derivatives. The Chatt and Shaw method has not been used for the preparation of  $\text{Ni}^{\text{II}}$  derivatives with acetylenic hydrocarbons containing two terminal  $\text{C}\equiv\text{CH}$  groups.

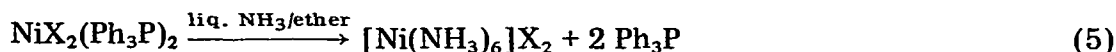
In our case the reaction between *trans*-[PdCl<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub>] and K<sub>2</sub>(*p*-PDE) proceeds according to eq. 3.



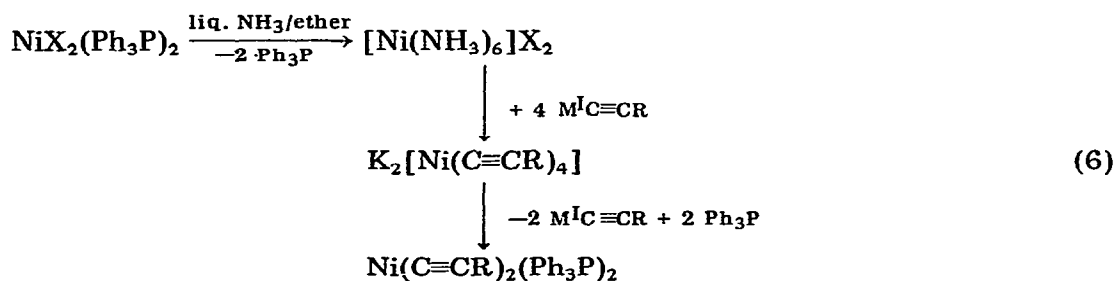
The analogous reaction with NiX<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub> (X = Cl, Br, I) complexes in liquid ammonia/ether always gives the homoleptic derivative I, according to eq. 4.



All attempts to obtain the desired product under a variety of conditions were unsuccessful. The differing reactivity of the MX<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub> (M = Ni, Pd) complexes towards the solvent (liquid ammonia/ether) may account for the observed behaviour. It is known [6] that PdCl<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub> dissolves only partially in this medium, whereas the NiX<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub> complexes (X = Cl, Br, I) undergo complete ammonolysis, according to eq. 5, yielding soluble products.



On this basis we can suppose that the formation of heteroleptic derivatives Ni(C≡CR)<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub> follows the sequence indicated in eq. 6, the homoleptic derivative being an intermediate. In the case of the *p*-PDE ligand the very low solubility of the homoleptic derivative would prevent the subsequent reaction step.



It should be noted that an excess of NaC≡CR (with no KC≡CR) was used in the reactions leading to heteroleptic complexes [Ni(C≡CR)<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub>] and that the sodium salts of the [Ni(C≡CR)<sub>4</sub>]<sup>2-</sup> anions are considerably more soluble in liquid ammonia/ether than the corresponding potassium salts.

In order to verify our proposed reaction scheme we carried out the Chatt and Shaw reaction [8] between NiCl<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub> and M<sup>I</sup>C≡CC<sub>6</sub>H<sub>5</sub> but using the potassium salt. A precipitate identified as the previously described K<sub>2</sub>[Ni(C≡CC<sub>6</sub>H<sub>5</sub>)<sub>4</sub>] [10] immediately appeared and Ph<sub>3</sub>P was recovered from the resulting solution. Upon stirring of the reaction mixture (without filtration) for 30 min the precipitate redissolves and [Ni(C≡CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub>] can be isolated, as described by Chatt and Shaw [8].

### *Stability of compounds*

All the compounds obtained were unstable towards oxidation and to hydrolysis, and the thermal stability was also low. The homoleptic Ni<sup>II</sup> compound is less stable than the Pd<sup>II</sup> complexes and the stabilities in the order  $K_4[\text{Pd}(p\text{-PDE})_2] < K_2[\text{Pd}(p\text{-PDE})_2] < K_2[\text{Pd}(p\text{-PDE})_2(\text{Ph}_3\text{P})_2]$  for the palladium derivatives.

All these compounds crystallize with lattice ammonia, which can be removed by exposure to a high vacuum for several hours at room-temperature, the complexes then becoming less stable.

The Ni<sup>II</sup> compound decomposes at room temperature, under dry N<sub>2</sub> after several days, its colour turning from yellow to grey. Handling causes it to become brownish.

The Pd<sup>II</sup> compounds are stable at room temperature under dry N<sub>2</sub> for several weeks, and are more stable the heteroleptic compound. The Pd<sup>0</sup> derivative is pyrophoric in air.

All the complexes are insoluble in organic solvents and decompose in water and dilute acids to give insoluble brown products. In concentrated acids they decompose immediately the reaction being violent in the case of the Ni<sup>II</sup> and Pd<sup>0</sup> derivatives.

The great unstability of these compounds is similar to that of the Ni and Pd homoleptic derivatives previously described [1]. However, the instability of the Pd<sup>II</sup> heteroleptic compound contrasts markedly with the stability of the heteroleptic derivatives of the type  $[\text{Pd}(\text{C}\equiv\text{CR})_2(\text{Ph}_3\text{P})_2]$  [8]. This lower stability may be due to the presence of the uncoordinated strongly basic alkynyl groups.

### *Infrared spectra and magnetic behaviour*

Table 1 lists the most significant IR frequencies of the new compounds. In an attempt to assign the  $\nu(\text{Ni}-\text{C}\equiv)$  stretching frequencies we prepared for comparison several known alkynyl complexes for which, however, this assignment had been not attempted.

The compounds, isolated as ammoniates, show the characteristic stretching and bending frequencies of NH<sub>3</sub> at 3300 and 1600 cm<sup>-1</sup>, respectively. All these compounds exhibit the internal vibrations of the *p*-PDE ligand, the most significant effect of the coordination being the shifts of the  $\nu(\text{C}\equiv\text{C})$  stretching bands towards higher frequencies than those for the free anionic ligand, which we assume to be present in Cs<sub>2</sub>(*p*-PDE) [11]. These  $\nu(\text{C}\equiv\text{C})$  frequencies values are always lower than that for the acetylenic hydrocarbon H<sub>2</sub>(*p*-PDE), which implies the presence of an additional  $d\pi-p\pi$  M → C bond. In the Pd complexes  $\nu(\text{C}\equiv\text{C})$  decreases with the oxidation state of metal, corresponding to a stronger  $\pi$ -back bonding M → C for the Pd<sup>0</sup> complex.

Tentative assignments of stretching frequencies  $\nu(\text{M}-\text{C}\equiv)$  have been made. Thus a shoulder in the range 553–549 cm<sup>-1</sup>, which appears on the strong acetylenic ligand band at 546 cm<sup>-1</sup> for the M<sup>II</sup> complexes, and a weak band at 560 cm<sup>-1</sup> in the Pd<sup>0</sup> complex have been tentatively assigned to  $\nu(\text{M}-\text{C}\equiv)$  stretching frequencies. The higher frequency value found for the Pd<sup>0</sup> complex may be related to a stronger  $d\pi-p\pi$  M → C bond.

All these complexes are diamagnetic, implying a planar geometry.

TABLE 1

PRINCIPAL INFRARED FREQUENCIES OF *p*-DIETHYNYLBENZENE (PDE) DERIVATIVES OF Ni<sup>II</sup>, Pd<sup>II</sup> AND Pd<sup>0</sup>

Compound	$\nu(\text{C}\equiv\text{C})$ ( $\text{cm}^{-1}$ )	$\nu(\text{M}-\text{C}\equiv)$ ( $\text{cm}^{-1}$ )
$\text{K}_2[\text{Ni}(p\text{-PDE})_2] \cdot 4 \text{NH}_3$	2059m	552(sh)
$\text{K}_2[\text{Pd}(p\text{-PDE})_2] \cdot 3 \text{NH}_3$	2074m	549(sh)
$\text{K}_4[\text{Pd}(p\text{-PDE})_2] \cdot 3 \text{NH}_3$	2050m	560w
$\text{K}_2[\text{Pd}(p\text{-PDE})_2(\text{Ph}_3\text{P})_2] \cdot 2 \text{NH}_3$	2073m	553(sh)
$\text{Cs}_2(p\text{-PDE})^a$	1994, 1977m	
$\text{K}_2[\text{Ni}(\text{C}\equiv\text{CC}_6\text{H}_5)_4]^b$	2066m	563w
$[\text{Ni}(\text{C}\equiv\text{CC}_6\text{H}_5)_2(\text{Ph}_3\text{P})_2]^c$	2095m	575m
$\text{K}_2[\text{Ni}(\text{C}\equiv\text{CH})_4] \cdot 2 \text{NH}_3^b$	1840, 1832s	516m

<sup>a</sup> From ref. 11. <sup>b</sup> From ref. 10. <sup>c</sup> From ref. 8. s, strong; m, medium; w, weak; sh, shoulder.

## Experimental

### Materials and methods

The reactions in liquid ammonia were carried out in a vacuum system similar to that described by Nast and Roos [12], in a rigorously moisture- and oxygen-free atmosphere. All solvents were purified and dried by conventional methods before use. *p*-Diethynylbenzene [13], Ni(NCS)<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub> [14], NiX<sub>2</sub>(Ph<sub>2</sub>P)<sub>2</sub> [15], Pd(CN)<sub>2</sub> and [Pd(CN)<sub>2</sub>en] [16] were prepared by literature methods. The alkaline salts of *p*-phenylenediethynyl were obtained as previously described [11].

Infrared spectra (4000–200 cm<sup>-1</sup>) were recorded on a Perkin Elmer 325 spectrophotometer, the samples being prepared under N<sub>2</sub> as Nujol mulls in a CsI cell.

Analyses for C and H were carried out on a Coleman Model 33 analyzer, K was determined by flame photometry, Ni by complexometry, and Pd gravimetrically as the diacetyldioximate. NH<sub>3</sub> was determined by the Kjeldahl method. Samples for metal determinations were dissolved in HClO<sub>4</sub>/HNO<sub>3</sub>.

### $\text{K}_2[\text{Ni}(p\text{-DPE})_2] \cdot 4 \text{NH}_3$ (I)

A filtered solution of Ni(NCS)<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub> (1.21 g, 5 mmol) in liquid NH<sub>3</sub> was added to a suspension of K<sub>2</sub>(*p*-PDE) (2.02 g, 10 mmol) in 150 ml of liquid NH<sub>3</sub>. A crystalline yellow solid was formed immediately. After several h at -70°C the precipitate was filtered off, washed several times with liquid NH<sub>3</sub> (30 ml each time) until the washings were colorless and then dried under high vacuum at -30°C, yielding 1.92 g (85%) of K<sub>2</sub>[Ni(*p*-PDE)<sub>2</sub>] · 4 NH<sub>3</sub>. (Found: C, 52.68; H, 3.62; N, 12.85; Ni, 12.81; K, 17.63. C<sub>20</sub>H<sub>20</sub>N<sub>4</sub>NiK<sub>2</sub> calcd.: C, 52.99; H, 4.41; N, 12.36; Ni, 12.96; K, 17.26%).

### $\text{K}_2[\text{Pd}(p\text{-PDE})_2] \cdot 3 \text{NH}_3$ (II)

A solution of Pd(CN)<sub>2</sub>en (1.00 g, 4.6 mmol) in liquid NH<sub>3</sub> was added to a suspension of K<sub>2</sub>(*p*-PDE) (1.86 g, 9.2 mmol) in ca. 120 ml of liquid NH<sub>3</sub>. After some minutes at -40°C with occasional stirring, the reaction mixture was maintained for several hours at -40°C until formation of a pale yellow, lamel-

lar solid, which was filtered off, freed from  $\text{CN}^-$  by washing with liquid  $\text{NH}_3$  (30 ml each time), and dried in a high vacuum at  $-40^\circ\text{C}$ , yielding 1.66 g (75%) of  $\text{K}_2[\text{Pd}(p\text{-PDE})_2] \cdot 3 \text{NH}_3$ . (Found: C, 48.87; H, 3.18; N, 8.23; Pd, 21.58; K, 15.89.  $\text{C}_{20}\text{H}_{17}\text{N}_3\text{PdK}_2$  calcd.: C, 49.62; H, 3.51; N, 8.68; Pd, 22.00; K, 16.16%).

*$\text{K}_4[\text{Pd}(p\text{-PDE})_2] \cdot 3 \text{NH}_3$  (III)*

A solution of potassium (4 mmol) in liquid  $\text{NH}_3$  (50 ml) was filtered into a suspension of II in liquid  $\text{NH}_3$  (100 ml). After a few minutes at the boiling temperature of  $\text{NH}_3$  followed by 24 h at  $-40^\circ\text{C}$  the intense blue coloration of solution disappears completely. The orange solid formed was filtered off, washed 3 times with 30 ml of liquid  $\text{NH}_3$ , and dried under high vacuum at  $-40^\circ\text{C}$ , yielding 0.84 g (60%) of  $\text{K}_4[\text{Pd}(p\text{-PDE})_2] \cdot 3 \text{NH}_3$  (III). (Found: N, 7.96; Pd, 18.72; K, 28.05.  $\text{C}_{20}\text{H}_{17}\text{N}_3\text{PdK}_4$  calcd.: N, 7.47; Pd, 18.94; K, 27.84%).

*$\text{K}_2[\text{Pd}(p\text{-PDE})_2(\text{Ph}_3\text{P})_2] \cdot 2 \text{NH}_3$  (IV)*

A solution of 1.01 g (5 mmol) of  $\text{K}_2(p\text{-PDE})$  in liquid ammonia (75 ml) was filtered into a solution of 0.40 g (1 mmol) of  $\text{PdCl}_2(\text{Ph}_3\text{P})_2$  in liquid  $\text{NH}_3$ . The mixture was stirred from time to time during several minutes and then kept at  $-40^\circ\text{C}$  for 5 h. The pale yellow solid formed was filtered off, washed 10 times with liquid  $\text{NH}_3$  (50 ml each time) and dried under a high vacuum, yielding 0.77 g (78%) of  $\text{K}_2[\text{Pd}(p\text{-PDE})_2(\text{Ph}_3\text{P})_2] \cdot 2 \text{NH}_3$ . (Found: C, 66.58; H, 4.26; N, 3.04; Pd, 11.30; K, 7.56.  $\text{C}_{56}\text{H}_{44}\text{P}_2\text{N}_2\text{PdK}_2$  calcd.: C, 67.87; H, 4.44; N, 2.82; Pd, 10.74; K, 7.89%).

*Reaction between  $\text{K}_2(p\text{-PDE})$  and  $\text{NiX}_2(\text{Ph}_3\text{P})_2$  compounds*

A suspension of 0.652 g (1 mmol) of  $\text{NiCl}_2(\text{Ph}_3\text{P})_2$  in cold dry diethyl ether (30 ml) was added dropwise with stirring to a suspension of 2.02 g (10 mmol) of  $\text{K}_2(p\text{-PDE})$  in 150 ml of liquid  $\text{NH}_3$ /Ether (4/1). A yellow solid separated. After 1 h at  $-50^\circ\text{C}$  with occasional stirring the liquid  $\text{NH}_3$  was evaporated off and 1 g of  $\text{NH}_4\text{Cl}$  was added to the residue. Addition of water to the ethereal solution caused a progressive disappearance of the yellow solid, with simultaneous formation of a dark brown, phosphine-free solid, with characteristics similar to those of the hydrolysis products of  $\text{K}_2[\text{Ni}(p\text{-PDE})_2]$ , while  $\text{Ph}_3\text{P}$  was recovered from the ethereal layer.

*Reaction between  $\text{KC}\equiv\text{CC}_6\text{H}_5$  and  $\text{NiX}_2(\text{Ph}_3\text{P})_2$*

A suspension of 0.652 g (1 mmol) of  $\text{NiCl}_2(\text{Ph}_3\text{P})_2$  in cold dry diethyl ether (30 ml) was added to a suspension of 1.39 g (10 mmol) of  $\text{KC}\equiv\text{CC}_6\text{H}_5$  in 150 ml of liquid  $\text{NH}_3$ /ether (4/1). A yellow solid separated, and was rapidly filtered off and identified as  $\text{K}_2[\text{Ni}(\text{C}\equiv\text{CC}_6\text{H}_5)_4]$ . If kept in contact with the solution this yellow solid redissolves after 1 h with occasional stirring. By addition of  $\text{NH}_4\text{Cl}$  (1 g) and water a second yellow solid, identified as  $\text{Ni}(\text{C}\equiv\text{CC}_6\text{H}_5)_2(\text{Ph}_3\text{P})_2$ , was isolated (25% yield) from the ethereal layer.

**Acknowledgement**

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