

Inorganica Chimica Acta 249 (1996) 237-238

Inorganica Chimica Acta

Note

Reaction of nickel(II) and palladium(II) with tetraphenyldiphosphine

Roberto Giannandrea^a, Piero Mastrorilli^a, Cosimo Francesco Nobile^{a,*}, Massimo Dilonardo^b

* Centro C.N.R. M.I.S.O. and Istituto di Chimica del Politecnico, trav. 200 Re David, 4 1-70126 Bari, Italy

^b Istituto di Chimica del Politecnico, trav. 200 Re David, 4 I-70126 Bari, Italy

Received 20 October 1995; revised 6 December 1995

Abstract

The reaction of tetraphenyldiphosphine with NiCl₂ and Pd(PhCN)₂Cl₂ was investigated. Aquo or alcohol complexes of nickel(II) chloride afforded Ni(PPh₂H)₄ whereas anhydrous NiCl₂ in aromatic solvents facilitated the decomposition of the diphosphine into triphenylphosphine and diphenylphosphine. Pd(PhCN)₂Cl₂ gave rise to Pd(Ph₂P-PPh₂)Cl₂.

Keywords: Nickel complexes; Palladium complexes; Diphosphine complexes

Following our studies on nickel-diphosphine complexes [1], we decided to investigate the behavior of nickel(II) and palladium(II) towards tetrasubstituted diphosphines.

In this note we describe the results obtained by reaction of nickel(II) and palladium(II) with tetraphenyldiphosphine (1) that led to a new synthesis of $Ni(PPh_2H)_4$ (2) and $Pd(Ph_2P-PPh_2)Cl_2$ (3).

The reaction between Ph_2P -PPh₂ and anhydrous NiCl₂ in toluene was carried out by Issleib and Schwager [2] and the formation of a dark solution was reported. No stable compound was isolated, thus suggesting the instability of the expected Ni(PPh₂-PPh₂)Cl₂ complex. We have carried out the same reaction in benzene and found that tetraphenyldiphosphine was slowly converted into triphenylphosphine and diphenylphosphine.

The simplest explanation of this finding might be the nickel-promoted reaction of tetraphenyldiphosphine with benzene summarized as:

 $Ph_2P-PPh_2 + PhH \rightarrow PPh_3 + PPh_2H$

but this hypothesis is to be discarded because of the lack of formation of any deuterated phosphorus compound from reaction of 1 and NiCl₂ in C₆D₆. The formation of PPh₃ and PPh₂H has to be regarded as the nickel-promoted decomposition of 1. In fact (i) the course of the reaction is the same using toluene instead of benzene; (ii) a variable amount of free diphenylphosphine and triphenylphosphine was found in all the reaction solutions involving nickel(II), described hereafter.

When NiCl₂· $6H_2O$ instead of anhydrous nickel chloride was reacted with 1 in toluene a reduction reaction occurred, leading to Ni(PPh₂H)₄ (2). Complex 2 was first isolated by Issleib and Wenschuh [3], but they mistook it for Ni(Ph₂PH)₂(PPh₂)₂; it was successively recognized and characterized by Bailey and co-workers [4].

A stoichiometric amount of diphenylphosphine oxide and HCl was found in the reaction mixture of $NiCl_2 \cdot 6H_2O$ and 1 thus validating the following reaction equation:

The presence of water is crucial for the reaction in that n supplies oxygen for the phosphine oxide and hydrogen for the coordinated diphenylphosphine.

Reaction (1) occurred much faster (~30 min) when hydrated nickel(II) chloride dissolved in ethanol was allowed to react with a toluene (or ethanolic) solution of 1. A new synthesis of 2 can thus be given as follows. An ethanolic solution of nickel(II) chloride hexahydrate (0.7 g, 2.95 mmol in 10 ml) was added dropwise to a stirred solution of tetraphenyldiphosphine (5.5 g, 14.9 mmol) in toluene (40 mi). After 30 min the initially brown solution lightened and 2 deposited as a yellow solid which was isolated by filtration, washed with ethanol and dried in vacuo (1.9 g, 80% yield). Its IR and UV-Vis features are the following: IR (nujol mull): 2248 (vs), 1092 (s), 846 (s), 746 (s), 733 (vs), 696 (vs), 503 (vs), 467 (s), 423 (s), 349 (w) cm⁻¹; UV-Vis (nujol mull): $\lambda = 361$, ~262 (sh) nm.

^{*} Corresponding author.

^{0020-1693/96/\$15.00 © 1996} Elsevier Science S.A. All rights reserved PII \$0020-1693(96)05086-4

The synthesis of Ni(PPh₂H)₄ car also be achieved by reaction of anhydrous NiCl₂ with λ in absolute ethanol. In this case the oxidized product was found to be PPh₂OEt and the stoichiometric equation becomes:

 $NiCl_2 \cdot 6EtOH + 5Ph_2P-PPh_2 \rightarrow$

 $Ni(PPh_2H)_4 + 6PPh_2OEt + 2HCl$

To the best of our knowledge the only reaction reported in the literature between Pd(II) and tetraphenyldiphosphine results in the formation of Pd[Ph₂P-PPh₂]₂Cl₂ [2]. The reaction was carried out by refluxing in benzene PdCl₂ with 1. We have found that by reacting Pd(PhCN)₂Cl₂ (1.27 g, 3.3 mmol) with tetraphenyldiphosphine (1.22 g, 3.3 mmol) in toluene (20+50 ml) at room temperature, a new orange complex is obtained that decomposes at 195 °C and whose elemental analyses are consistent with the formula $Pd(Ph_2P-PPh_2)Cl_2$ (3) (isolated yield = 83%).

Its IR spectrum in nujol exhibits bands at 3055, 2927, 1432, 1088, 741, 691, 502, 493 cm⁻¹ whereas its UV–Vis spectrum in methylene chloride shows a peak at 228 nm (ϵ =43 180) and four shoulders at 395, 331, 286 and 251 nm. Its ³¹P NMR spectrum consists of a singlet at 76.4 ppm (from ext. 85% H₃PO₄, solvent CDCl₃).

References

- [1] P. Mastrorilli, G. Moro, C.F. Nobile and M. Latronico, Inorg. Chim. Acta, 192 (1992) 183; A. Sacco and P. Mastrorilli, J. Chem. Soc., Dalton Trans. (1994) 2761.
- [2] K. Issleib and G. Schwager, Z. Anorg. Allg. Chem., 310 (1961) 43.
- [3] K. Issleib and E. Wenschuh, Z. Anorg. Allg. Chem., 305 (1960) 15.
- [4] C.W. Weston, G.W. Bailey, J.H. Nelson and H.B. Jonassen, J. Inorg. Nucl. Chem., 34 (1972) 1752.