Inorganica Chimica Acta, 24 (1977) L25–L26
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Ammonation Reactions of Dihalo (or Pseudohalo) Bis(tertiary phosphine) Nickel(II) Complexes in Liquid Ammonia/Ether

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Received May 27, 1977

The $[NiX_2(R_3P)_2]$ complexes (X = halide or pseudohalide, R = alkyl, aryl) are starting substances for the synthesis of bis(alkynyl)bis(tertiary phosphine) nickel(II) complexes in liquid ammonia/diethyl ether as solvent [1, 2]. In the tentative synthesis of some of these alkynyl complexes [3] unexpected results have led us to the study of the possible interactions between the starting compounds and the reaction medium. Ammonation reactions of Ni(II) salts of the type NiX_2 ($X = I^-, IO_3^-$) in liquid ammonia have been described in the literature [4, 5].

It is well known that the reaction of *trans*-$[NiX_2(R_3P)_2]$ (R = alkyl) with ethyl- and butylamine leads to a fast replacement of the ligand amine by phosphine when X = halide or SCN^- [6]. The substitution rate is considerably smaller for $X = CN^-$ and in the reaction of *trans*-$[Ni(CN)_2\{(C_2H_5)(C_6H_5)_2P\}_2]$ with butylamine a pentaccordinated species has been spectrophotometrically detected [6]. Other reaction products have not been described.

In this work we describe the behaviour of tetrahedral complexes $[NiX_2(Ph_3P)_2]$ (X = Cl, Br, I) and square planar complexes *trans*-$[Ni(CN)_2(R_3P)_2]$ (X = CN, NCS; R = Ph and X = Cl, CN; R = n-Bu) in liquid ammonia/ether as solvent.

The complexes have been obtained by addition of phosphine to the corresponding Ni(II) salt in different solvents as reported in the literature [1, 2]. The reaction takes place by condensation of liquid ammonia on a suspension or solution of the Ni(II) complex in dehydrated ether up to a volume rate liquid NH_3/ether = 3/1. After stirring for 2 hr, the liquid NH_3 is evaporated, the solids of the ether phase filtered and the dissolved products isolated by distillation of the solvent. Our results of the ammonation reactions are given in Table I.

In the $[NiX_2(R_3P)_2]$ compounds (X = Cl, Br, I; R = Ph or X = Cl; R = n-Bu) the formation of $[Ni(NH_3)_6]X_2$ with quantitative yield always takes place. For *trans*-$Ni(CN)_2(Ph_3P)_2]$ the polymeric species $Ni(CN)_2(NH_3)$ is quantitatively obtained. However, for *trans*-$[Ni(CN)_2(n\text{-}Bu_3P)_2]$, after 48 hr the formation of $Ni(CN)_2(NH_3)$ occurs with a yield of 15% only. In this last case a deep red colour that appeared in the reaction medium was thought to be due to the pentacoordinated species $[Ni(CN)_2(n\text{-}Bu_3)_3]$, whose stability increases when the temperature decreases [7]. After evaporation of NH_3 it has been shown spectrophotometrically that the *trans*-$[Ni(CN)_2(n\text{-}Bu_3P)_2]$ and $[Ni(CN)_2(n\text{-}Bu_3P)_3]$ species are present in the organic solvent. This behaviour of the *trans*-$[Ni(CN)_2(n\text{-}Bu_3)_2]$ complex in liquid ammonia/ether is similar to that found for *trans*-$[Ni(CN)_2\{(C_2H_5)(C_6H_5)_2P\}_2]$ when ethyl- and butylamine are added to an organic solution containing the complex [6]. In our case, even with a low yield, a total substitution of the phosphine ligands takes place, with formation of the octahedral polymeric complex $Ni(CN)_2(NH_3)$. On the other hand, the *trans*-$[Ni(CN)_2(Ph_3P)_2]$ undergoes an instantaneous and complete reaction with loss of the phosphine ligand and formation of $Ni(CN)_2(NH_3)$. This different behaviour can be interpreted taking into account the different tendencies of the two phosphines with respect to the formation of pentacoordinated species, that of $n\text{-}Bu_3P$ being much greater than that of Ph_3P [8]. Hitherto the pentacoordinated complex $[Ni(CN)_2(Ph_3P)_3]$ has been neither isolated nor spectrophotometrically detected. This fact has been attributed to a conjunction of electronic and steric effects [9–11].

In the reaction of *trans*-$[Ni(NCS)_2(Ph_3P)_2]$ both Ni–P bonds are broken with simultaneous formation of $[Ni(NCS)_2(NH_3)_4]$. Pentacoordinated species were not observed in this reaction. This fact can be easily justified taking into account that the tendency to the formation of $[NiX_2(R_3P)_3]$ complexes is considered to depend more on the anion polarizability than on its position in the spectrochemical series [11].

The ammonation reaction of *trans*-$[NiCl_2(n\text{-}Bu_3P)_2]$ is analogous to that of *trans*-$[Ni(NCS)_2(Ph_3P)_2]$ in spite of the greater ability of $n\text{-}Bu_3P$ to stabilize pentacoordinate species. This fact can be due to the relatively low polarizability of Cl^-. The low tendency of the tetrahedral complexes $[NiX_2(Ph_3P)_2]$ (X = Cl, Br, I) to form pentacoordinated species, except in the case of some phosphines such as Me_3P and Me_2PhP [11, 12] can account for their fast ammonation reactions.

It is noticeable that the analogous *trans*-$[PdCl_2(Ph_3P)_2]$ palladium(II) complex does not react under the same conditions as the corresponding Ni(II) compound, even after a long reaction time. This can be due to a stronger interaction between the soft cation Pd(II) and the soft ligand phosphine between the hard cation Ni(II) and the same ligand, according to Pearson's classification.

TABLE I. Products, Characterization Methods, Reaction Times and Yields for Ammonation Reactions of $[NiX_2(R_3P)_2]$ Complexes.

Complex	Reaction Products	Characterization Method	Time	Yield (%)
$[NiX_2(Ph_3P)_2]$ (X = Cl, Br, I)	$[Ni(NH_3)_6]X_2$ $+ Ph_3P$	a, b b, c	inst.[f]	100
trans-$[NiCl_2(n\text{-}Bu_3P)_2]$	$[Ni(NH_3)_6]Cl_2$ $+ n\text{-}Bu_3P$	a, b b	inst.	100
trans-$[Ni(NCS)_2(Ph_3P)_2]$	$[Ni(NCS)_2(NH_3)_4]$ $+ Ph_3P$	a,b b, c	inst.	100
trans-$[Ni(CN)_2(Ph_3P)_2]$	$Ni(CN)_2(NH_3)$	a, d	inst.	100
trans-$[Ni(CN)_2(n\text{-}Bu_3P)_2]$	$Ni(CN)_2(NH_3)$ $+ [Ni(CN)_2(n\text{-}Bu_3P)_2]$ $+ [Ni(CN)_2(n\text{-}Bu_3P)_3]$	a, d e e	48 hr.	15

[a] Chemical analysis. [b] I.r. spectrum. [c] Melting point. [d] X-ray powder diffraction pattern. [e] UV and visible spectrum.
[f] Inst. = instantaneous.

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