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Dicyclohexylphosphido Complexes of Nickel(I)

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The reduction of $NiCl_2(PCy_2Ph)_2$ with Na in toluene under N_2 gives the dimeric Ni(I) phosphido-complex $[Ni(\mu\text{-}PCy_2)(PCy_2Ph)]_2$, while the same reaction carried out under CO gives the Ni(0) carbonyl-complex $Ni(PCy_2Ph)_2(CO)_2$. The CO displaces the phosphine ligand from the Ni(I) phosphido-complex, affording the dimeric Ni(I) phosphido–carbonyl-complex $[Ni(\mu\text{-}PCy_2)(CO)_2]_2$.

A mechanism for the reaction leading to the dimeric Ni(I) phosphido-complex is suggested.

Introduction

Nickel(I) compounds are not very common and, among them, the phosphido-complexes are very rare. To our knowledge only two such compounds have been reported in the literature: the well characterized $[Ni(PPh_2)(CO)_2]_2$, obtained from $Ni(CO)_4$ and $Ph_2P–PPh_2$ [1], and the $[Ni(PPh_2)(PPh_3)]_2$, obtained as a black precipitate from $Ni(PPh_3)_3$ solutions on standing, but not fully characterized [2].

In the pursuit of our studies on the preparation of Ni(0) and Ni(I) compounds [3, 4], we describe in this paper, beside a new carbonyl–phosphido-complex of Ni(I) and a carbonyl–phosphine-complex of Ni(0), the first well characterized phosphido-complex of Ni(I) in which the nickel is bound only to phosphorous ligands, namely $[Ni(\mu\text{-}PCy_2)(PCy_2Ph)]_2$, which has been obtained quite unexpectedly through a reaction which usually gives halo-compounds of Ni(I) or Ni(0) derivatives [3].

Experimental

All preparations were carried out in deoxygenated solvents and all operations were routinely performed in an atmosphere of purified nitrogen using standard Schlenk techniques. Samples for melting point were contained in tubes sealed under nitrogen. Infrared spectra were recorded on a Perkin-Elmer 577 instrument and the electronic spectra were recorded on a Varian Cary 219 spectrophotometer. Gas chromatographic determinations were carried out on EGSSX and Porapak Q columns using a Hewlett-Packard 5750 apparatus. Magnetic susceptibilities were measured under a nitrogen atmosphere by the Faraday method as previously described [5].

Di-μ-(dicyclohexylphosphido)bis(dicyclohexylphenylphosphinenickel)

A suspension of $NiCl_2(PCy_2Ph)_2$ (3.0 g, 4.4 mmol) and sodium sand (0.53 g, 23.0 mmol) in toluene (30 ml) was stirred at room temperature until a deep red solution was obtained (about 15 h) and then stirred for a further 15 h. The filtered solution was concentrated *in vacuo* to about 5 ml and, after addition of n-pentane (15 ml), cooled to –30 °C. The dark red crystals formed on standing (*ca.* 12 h) were filtered off, washed with cold n-pentane and dried *in vacuo*. Yield 1.4 g (60%). Mp 221–223 °C. The compound is soluble in aromatic solvents and in THF, slightly soluble in n-pentane, insoluble in ethanol, acetone and diethyl ether. It was oxidized by air, slowly in the solid state and quickly in solution. Magnetic moment: μ = 1.89 B.M. at 25 °C; μ = 1.36 B.M. at –195 °C. *Anal.* Calcd for $C_{60}H_{98}P_4Ni_2$: C, 67.94; H, 9.31; P, 11.68; Ni, 11.07. Found: C, 64.8; H, 9.0; P, 11.6; Ni, 11.0%.

The gas chromatographic analysis of the mother liquors showed the presence of diphenyl (0.30 g, 88%).

Di-μ-(dicyclohexylphosphido)bis(dicarbonylnickel)

Carbon monoxide was bubbled under stirring into a suspension of 0.650 g (0.61 mmol) of $[Ni(PCy_2)(PCy_2Ph)]_2$ in 50 ml of n-pentane at room temperature. The reaction mixture turned into a red-brown solution (*ca.* 30 minutes), which was concentrated *in vacuo* to about 10 ml and cooled to –20 °C. The dark red-brown crystals formed on standing were filtered off, washed with cold n-pentane and dried *in vacuo*. Yield 0.29 g (76%). The compound was recrystallized from benzene by adding ethanol. Mp 184–186 °C. The compound is diamagentic (μ = 0.46 B.M. at 25 °C), very soluble in toluene, benzene, THF, CH_2Cl_2, slightly soluble in n-pentane and diethyl ether, insoluble in ethanol. It is very

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slowly oxidized by air in the solid state and decomposes in concentrated sulfuric acid giving off CO quantitatively (detected by gas chromatography). *Anal.* Calcd for $C_{28}H_{44}O_4P_2Ni_2$: P, 9.93; Ni, 18.81; CO, 17.96. Found P, 9.80; Ni, 18.5; CO, 17.3%.

Bis(dicyclohexylphenilphosphine)dicarbonilnickel

Carbon monoxide was introduced under stirring at room temperature into a suspension of $NiCl_2(PCy_2Ph)_2$ (0.30 g, 0.44 mmol) and sodium sand (50 mg, 2.2 mmol) in 15 ml of toluene. As soon as the initially red mixture turned into a colourless solution (*ca.* 5 h), the metallic sodium in excess was filtered out under nitrogen and the solution was concentrated *in vacuo* to about 4 ml. On adding ethanol (6 ml) and cooling to −20 °C, white crystals were obtained. Yield 0.215 g (74%). M.p. 178–180 °C. The compound was soluble in toluene, benzene, THF, very slightly soluble in ethanol. *Anal.* Calcd for $C_{38}H_{54}O_2P_2Ni$: P, 9.34; Ni, 8.85. Found P, 9.32; Ni, 8.80%.

Results and Discussion

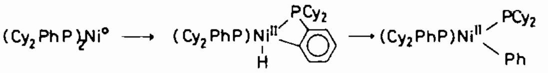
As we have shown in previous reports [3, 4], the tertiary phosphine complexes of Ni(II), $NiX_2(PR_3)_2$ (X = Cl, Br), can be easily reduced with metals (Zn or Na) to Ni(0) derivatives, and the reduction of the complexes of basic and bulky phosphines, such as PCy_3, can be stopped at the intermediate Ni(I) complexes $[NiX(PCy_3)_2]_2$. We have now found that the reduction of $NiCl_2(PCy_2Ph)_2$ with sodium in toluene at room temperature gives the Ni(I) bicyclohexylphosphido-complex $[Ni(\mu\text{-}PCy_2)(PCy_2Ph)]_2$ according to the equation:

$$2NiCl_2(PCy_2Ph)_2 + 4Na \rightarrow [Ni(\mu\text{-}PCy_2)(PCy_2Ph)]_2 + Ph_2 + 4NaCl \qquad (1)$$

The reaction proceeds through the formation of an unstable Ni(0) complex, $Ni(PCy_2Ph)_2$, which, unlike the corresponding tricyclohexylphosphine compound [3], does not stabilize by reaction with dinitrogen and decomposes to the final products, probably through the formation of an unstable Ni(II) intermediate according to the sequence:

$$Ni^0(PCy_2Ph)_2 \rightarrow Ni^{II}(Ph)(PCy_2)(PCy_2Ph) \rightarrow \tfrac{1}{2}[Ni(PCy_2)(PCy_2Ph)]_2 + \tfrac{1}{2}Ph_2 \qquad (2)$$

The formation of a Ni(0) complex as the first step of the reaction is confirmed by the fact that the same reaction carried out in the same conditions but under a carbon monoxide atmosphere gives the Ni(0) complex $Ni(CO)_2(PCy_2Ph)_2$ in very good yields. An intramolecular rearrangement of the coordinatively unsaturated Ni(0) compound, proceeding through a metal–carbon bond formation and then a cleavage of the strained phosphorus–carbon bond as already observed in tertiary phosphine complexes of transition metals [6], can easily occur according to the sequence



(3)

It is known that the stability of the tertiary phosphine arylnickel(II) complexes of the type $(R_3P)_2Ni(aryl)X$ strongly depends on the nature of the X ligand [7] and that unsaturated tertiary phosphine–nickel(0) compounds promote coupling reactions of aromatic halides to give biaryl in high yields [8]. However, the conversion of a coordinatively unsaturated dicyclohexylphosphidophenylnickel(II) intermediate to the final products can occur through several mechanistic pathways and speculation would be premature until further studies have been made. The Ni(I) phosphido-complex $[Ni(\mu\text{-}PCy_2)(PCy_2Ph)]_2$ is a dark red crystalline compound, unstable to the air. Its magnetic moment at room temperature (1.89 B.M.) is smaller than that usually observed for Ni(I) complexes which do not show any Ni–Ni interaction, and decreases further at low temperature (1.36 B.M. at −195 °C), suggesting some intramolecular antiferromagnetic exchange coupling between the two nickel atoms. It easily reacts with carbon monoxide to give the diamagnetic (μ = 0.46 B.M. at 25 °C) Ni(I) phosphido-complex $[Ni(PCy_2)(CO)_2]_2$, which shows in its infrared spectrum (Table I) carbonyl stretching frequencies very similar to those shown by the corresponding $[Ni(PPh_2)(CO)_2]_2$. It reacts also with hydrogen in toluene giving an orange solution which shows in its infrared spectrum an absorption band at 2322 cm^{-1}, ascribable to a P–H stretching. How-

TABLE I. Infrared Spectral Data.

Complex	Solvent	ν(CO)cm^{-1}
$[Ni(PCy_2)(CO)_2]_2$	Pentane	2070(w), 2016(vs), 1986(vs)
$[Ni(PCy_2)(CO)_2]_2$	Nujol mull	2016(vs), 1975(vs)
$Ni(PPhCy_2)_2(CO)_2$	Toluene	1982(vs), 1918(vs)
$Ni(PPhCy_2)_2(CO)_2$	Nujol mull	1988(vs), 1926(vs)
$Ni(PPhCy_2)_2(CO)_2$ + CO	Toluene	2065(s), 1982(vs), 1918(m)
$[Ni(PPh_2)(CO)_2]_2$[a]	CS_2	2032(vs), 2003(vs)

[a] From ref. 1.

TABLE II. Electronic Spectral Data.

Complex	Solvent	$\lambda^a(\epsilon)^b$
$[Ni(PCy_2)(PPhCy_2)]_2$	Toluene	275(1790), 340(3410), 380(3130), 526(490)
$[Ni(PCy_2)(CO)_2]_2$	Toluene	302(2818), 367(2284), 446(2172), 560(sh)(190)
$Ni(PCy_3)_2Cl^c$	Benzene	290(1260), 340(2490), 360(2435), 400(600)
$[Ni(PCy_3)_2Cl]_2{}^c$	Solid	345(sh), 370, 500(br)
$[Ag(dipy)_2]S_2O_8{}^d$	Water	357(>2300), 454(~1600)

^{a}Wavelength maxima in nm. ^{b}Extinction coefficient in $cm^{-1}M^{-1}$. ^{c}From ref. 3. ^{d}From ref. 9.

ever, we were not able to obtain any well characterized compound from this solution.

The electronic spectrum (Table II) of $[Ni(\mu\text{-}PCy_2)(PCy_2Ph)]_2$ closely corrsponds to those of tricoordinated Ni(I) complexes [3], while that of $[Ni(\mu\text{-}PCy_2)(CO)_2]_2$ is very similar to those of tetracoordinate Ni(I) [3] or Ag(II) complexes [9], confirming the dimeric structure assigned to these compounds.

The Ni(0) complex $Ni(PCy_2Ph)_2(CO)_2$ shows in its infrared spectrum (Table I) two equally strong absorption bands due to the CO stretching, as usually shown by the substituted nickel–carbonyl complexes of C_{2v} symmetry. In toluene solution under carbon monoxide it shows a new band at 2065 cm^{-1}, as well as an increase of the intensity of the band at 1982 cm^{-1} and a decrease of the intensity of the band at 19818^{-1}. By the method of Timney [10] for predicting the carbonyl stretching frequencies in transition metal compounds, we have calculated, from the stretching frequencies of $Ni(PCy_2Ph)_2(CO)_2$ in toluene, a ligand effect constant value of -55.6 Nm^{-1} for the tetrahedrally bound PCy_2Ph. From this value, a carbonyl stretching force constant of 1629 Nm^{-1} and a CO–CO interaction force constant of 42.9 Nm^{-1} have been calculated for the complex $Ni(PCy_2Ph)(CO)_3$ and finally, using the methods of Haas and Sheline [11], the carbonyl stretching frequencies of 1982 cm^{-1} and 2061 cm^{-1} have been calculated for this latter compound. These values agree very well with those shown by the $Ni(PCy_2Ph)_2(CO)_2$ solution in the presence of carbon monoxide, confirming that the carbon monoxide easily displaces the phosphine ligand from the $Ni(PCy_2Ph)_2(CO)_2$, giving rise in solution to the equilibrium:

$$Ni(PCy_2Ph)_2(CO)_2 + CO \rightleftarrows Ni(PCy_2Ph)(CO)_3 + PCy_2Ph \qquad (4)$$

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