Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

π-CYCLOPENTADIENYLS OF NICKEL(II)

III. REACTION OF π-CYCLOPENTADIENYLBIS(TRI-n-BUTYLPHOSPHINE)NICKEL CHLORIDE WITH VARIOUS ANIONS (X^-) IN AQUEOUS SOLUTION: FORMATION OF NOVEL π-$C_5H_5NiXPBu_3$

MASAO SATO, FUMIE SATO AND TADAO YOSHIDA
Department of Chemical Engineering, Tokyo Institute of Technology, Tokyo (Japan)

(Received March 24th, 1971)

SUMMARY

The ionic nickel complex π-cyclopentadienylbis(tri-n-butylphosphine)nickel chloride (I) has been treated with various anions X^- in aqueous solution to give the complexes $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+X^-$ (II) ($X=NCO$, NCS, N_3, ClO_4, ClO_3, NO_3 and NO_2).

Except when $X=ClO_4$ or NO_3, the complexes (II) dissociate in non-polar solvents, such as benzene, or above their melting points according to the following equation:

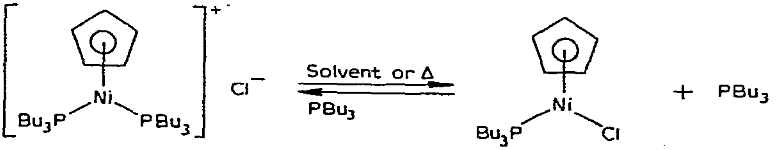
$$\underset{\text{(II)}}{[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+X^-} \underset{PBu_3}{\overset{\text{Solvent or }\Delta}{\rightleftharpoons}} \underset{\text{(III)}}{\pi\text{-}C_5H_5NiX\cdot PBu_3} + PBu_3$$

The complexes of type (III) with $X=NCO$ and NCS were obtained by the pyrolysis of the corresponding complex (II).

In the case of $X=CN$ and SH, (I) gave the complexes (III) directly.

INTRODUCTION

Recently we obtained the ionic organonickel complex, π-cyclopentadienylbis(tri-n-butylphosphine)nickel chloride (I), and found that (I) is dissociated in non-polar solvents such as benzene, or above its melting point according to the equation[1].



In view of the above equation, it might be expected that we could produce the covalent complexes $\pi\text{-}C_5H_5NiX\cdot PBu_3$ by the pyrolysis of the ionic complexes $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+X^-$ which are obtainable by the treatment of (I) with various anions X^- in aqueous solution.

TABLE 1

PROPERTIES AND ANALYTICAL DATA OF COMPLEXES $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+X^-$ AND $\pi\text{-}C_5H_5NiX \cdot PBu_3$

Complex	Colour	M.p. (°C)	Proton NMR data		IR data (cm^{-1})	Mol.wt. found (calcd.)	Colour of benzene solution
			$\tau(\pi\text{-}C_5H_5)$	$\tau(PBu_3)$			
$\pi\text{-}C_5H_5NiCN \cdot PBu_3$	Green	94–95	4.92(5)	7.8–9.3(27)^a	ν(C=N)2125	352(352)	
$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+NCS^-$	Green	68–70 (dec.)	4.84(5)	7.6–9.2(54)^a	ν(C=N)2060		Brown
$\pi\text{-}C_5H_5NiNCS \cdot PBu_3$	Reddish brown	99–100	4.80(5)	7.8–9.3(27)^a	ν(C=N)2070 ν(C–S) 820	390(384)	
$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+NCO^-$	Greenish yellow	57–58 (dec.)	4.93(5)	7.7–9.2(54)^a	ν(C=N)2140, 2160		Red
$\pi\text{-}C_5H_5NiNCO \cdot PBu_3$	Red	66–67	4.94(5)	7.8–9.3(27)^a	ν(C=N)2250		
$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+N_3^-$	Greenish yellow	77–79 (dec.)	4.71(5)	7.2–9.3(54)^a	ν(N=N=N)2001		Red
$\pi\text{-}C_5H_5NiSH \cdot PBu_3$	Reddish brown	51–52	5.00(5)	7.7–9.3(27)^a τ(SH)4.75(1)	ν(S–H)2500–2700	348(359)	
$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+ClO_4^-$	Green	113–115 (dec.)	4.47(5)	8.0–9.15(54)^b	ν(ClO_4^-)613, 1080	627(627)	Green
$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+ClO_3^-$	Green	117–118 (dec.)	4.45(5)	8.0–9.2(54)^b	ν(ClO_3^-)470, 595 965	438(611)	Reddish brown
$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+NO_3^-$	Greenish yellow	164–165 (dec.)	4.46(5)	8.0–9.15(54)^b	ν(NO_3^-)1330–1390	558(590)	Green
$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+NO_2^-$	Green	85–87 (dec.)	4.75(5)	9.5–9.4(54)^a	ν(NO_2^-)1210, 1270	270(574)	Reddish brown

[a] Spectra were run in CS_2. [b] Spectra were run in CD_3COD.

RESULTS AND DISCUSSION

Complex (I) readily reacts with sodium or potassium salts in aqueous solution to undergo two types of reaction. With NaNCO, KNCS, NaN_3, $NaClO_4$, $NaClO_3$, $NaNO_3$ and $NaNO_2$, anion exchange occurs, as in eqn. (1):

$$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^- + MX \rightarrow [\pi\text{-}C_5H_5Ni(PBu_3)_2]^+X^- + MCl \qquad (1)$$

$$(M = Na, K; X = NCO, NCS, N_3, ClO_4, ClO_3, NO_3, NO_2)$$

With NaCN and NaSH, on the other hand, the covalent complexes π-C_5H_5-$NiCN \cdot PBu_3$ and π-$C_5H_5NiSH \cdot PBu_3$ are produced, anion-exchanged products no doubt being intermediates, as in eqn. (2):

$$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^- + NaX \rightarrow [\pi\text{-}C_5H_5Ni(PBu_3)_2]^+X^- + NaCl \rightarrow \pi\text{-}C_5H_5NiX \cdot PBu_3 + PBu_3 \qquad (2)$$

$$(X = CN, SH)$$

From the colour of the benzene solution of the ionic complexes, the apparent molecular weights determined by cryoscopy in benzene and the colour change above the melting point, it was deduced that the ionic complexes were in equilibrium with covalent complexes in non-polar solvents or above their melting points, as represented in eqn. (3):

$$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+X^- \rightleftharpoons \pi\text{-}C_5H_5NiX \cdot PBu_3 + PBu_3 \qquad (3)$$

$$(X = NCO, NCS, N_3, ClO_3, NO_2)$$

Indeed, we were able to obtain the covalent complexes π-$C_5H_5NiNCO \cdot PBu_3$ and π-$C_5H_5NiNCS \cdot PBu_3$ by pyrolysis of the ionic complexes $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+$-$NCO^-$ and $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+NCS^-$.

Some properties of the new complexes obtained are listed in Table 1.

The covalent complex in which X = NCS has an IR band at 2070 cm^{-1} attributable to ν(C=N), and one at 820 cm^{-1} attributable to ν(C–S). These results indicate that the complex is isothiocyanate[2]. The complex in which X = SH has an IR band at 2500–2700 cm^{-1} attributable to ν(S–H), and a NMR band at τ 4.75 attributable to the proton of an SH group. The complex, π-$C_5H_5NiSH \cdot PBu_3$, seems to be the first example of organonickel compound which has a direct bond between the metal and an SH group.

The most striking difference between the IR spectra of the ionic and covalent complexes is that the strong out-of-plane deformation band of the π-cyclopentadienyl for the former appears at a frequency above 800 cm^{-1} and for the latter it appears at below 800 cm^{-1}.

Except for that in which X = NCO, the ionic complexes are stable in the air as solids, and the covalent complexes in which X = CN, NCS, NCO are stable under nitrogen, but the compound with X = SH is slowly decomposed at room temperature.

EXPERIMENTAL

$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ was prepared as previously described[1]. Benzene, n-hexane and water were purified in the usual ways and degassed before use. IR spectra were recorded on a JASCO IR-G spectrometer. Proton NMR spectra were recorded on a JEOL-JNM-4H-100-NMR spectrometer with TMS as internal standard. All experiments were conducted under dry nitrogen.

Reaction of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ *with NaCN*

3 mmoles of NaCN in 20 ml of water were added to a solution of 1 mmole of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ in 50 ml of water at room temperature. Reaction occurred immediately, and a green oil appeared. This was extracted with 50 ml of benzene, and benzene solution was dried over anhydrous calcium chloride. The solution was evaporated *in vacuo* and the residue was recrystallized from a benzene/n-hexane mixture to give green crystals, m.p. 94–95°, in 92% yield. (Found: C, 61.67; H, 9.34; N, 3.90; mol.wt. cryoscopic in benzene, 352. $C_{18}H_{32}NNiP$ calcd.: C, 61.50; H, 9.10; N, 3.98%; mol.wt., 352.)

Reaction of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ *with NaSH*

When 3 mmoles of NaSH in 20 ml of water was added to a solution of 1 mmole of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ in 50 ml of water at room temperature, a brown oil immediately appeared. This was extracted with 50 ml of benzene, and the benzene solution was dried over anhydrous calcium chloride. The solution was evaporated *in vacuo* and the residue was recrystallized from n-pentane to give brown crystals, m.p. 51–52°, in 90% yield. (Found: C, 56.77; H, 9.32; S, 8.28; mol.wt. cryoscopic in benzene, 348. $C_{17}H_{33}NiSP$ calcd.: C, 56.20; H, 9.20; S, 8.90%; mol.wt. 359.)

Reaction of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ *with NaNCO*

When 3 mmoles of NaNCO in 20 ml of water was added at room temperature to a solution of 1 mmole of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ in 50 ml of water a greenish-brown precipitate immediately appeared. This was extracted with 50 ml of benzene, and the benzene solution was dried over anhydrous calcium chloride. The solution was evaporated *in vacuo* and the residue was recrystallized from n-hexane in the presence of tri-n-butylphosphine to give green crystals, m.p. 57–58° (decompn.), (Found: C, 62.63; H, 10.44; N, 2.29. $C_{30}H_{59}NNiOP_2$ calcd.: C, 63.19; H, 10.35; N, 2.45%.)

Pyrolysis of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+NCO^-$

$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+NCO^-$ was heated at 30° under vacuum. The colour changed from green to reddish brown, and recrystallization from n-hexane gave reddish brown crystals, m.p. 66–67°, in 50% yield. (Found: C, 58.44; H, 8.97; N, 3.62. $C_{18}H_{32}NNiOP$ calcd.: C, 58.70; H, 8.70; N, 3.80%.)

Reaction of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ *with KNCS*

When 3 mmoles of KNCS in 20 ml of water was added at room temperature to a solution of 1 mmole of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ in 50 ml of water a green precipitate appeared. This was extracted with 50 ml of benzene and the benzene solution was dried over anhydrous calcium chloride. The solution was evaporated *in vacuo* and the residue was recrystallized from a benzene/n-hexane mixture to give green crystals, m.p. 68–70° (decompn.) (Found: C, 62.47; H, 10.45; N, 2.62. $C_{30}H_{59}NNiP_2S$ calcd.: C, 61.45; H, 10.05; N, 2.39%.)

Pyrolysis of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+NCS^-$

$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+NCS^-$ was heated at 60–70° under vacuum for 5 h. The

TABLE 2

NaX	Reaction condition	Yield (%)	Analysis found (calcd.) (%)			
			C	H	N	Cl
NaN_3	At 0°	84	61.15 (61.10)	10.59 (10.35)	7.38 (7.35)	
$NaClO_4$	At room temp.	82	55.69 (56.38)	9.67 (9.57)		
$NaClO_3$	At room temp.	87	57.45 (57.88)	9.81 (9.81)		5.51 (5.91)
$NaNO_3$	At room temp.	86	58.04 (58.95)	9.84 (10.00)	2.51 (2.38)	
$NaNO_2$	At room temp.	91	59.81 (60.58)	10.58 (10.29)	2.53 (2.46)	

colour changed from green to brown and recrystallization from a benzene/n-hexane mixture gave reddish brown crystals (quantitatively), m.p. 99–100°. (Found: C, 55.88; H, 8.26; N, 3.59; mol.wt. cryoscopic in benzene, 390. $C_{18}H_{32}NPSNi$ calcd.: C, 56.38; H, 8.35; N, 3.67%; mol.wt., 384.)

The reaction conditions, yields, and analyses of the other ionic complexes are given in Table 2.

REFERENCES

1 M. Sato, F. Sato and T. Yoshida, *J. Organometal. Chem.*, 26 (1971) C49.
2 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*. Wiley, New York, 1970.