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π-CYCLOPENTADIENYLBIS(TRI-n-BUTYLPHOSPHINE)NICKEL HALIDE

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SUMMARY

The reaction of nickelocene (dicyclopentadienylnickel) with allyl halide in the presence of tri-n-butylphosphine has been shown to produce π-cyclopentadienyl-bis(tri-n-butylphosphine)nickel halide.

INTRODUCTION

The complexes π-$C_5H_5Ni(Ph_3P)_2F$, $[\pi$-$C_5H_5Ni(Ph_3P)_2]^+SnCl_3^-$, and $[\pi$-$C_5H_5Ni(Ph_3P)_2]^+ SnCl_3^- \cdot Y$, where Y = CH_2Cl_2 or $(CH_3)_2CO$ have been described recently[1,2], but no other complexes of this type are known. This paper describes the preparation of $\{\pi$-$C_5H_5Ni[P(n\text{-}Bu)_3]_2\}^+X^-$ (X = Cl, Br, I).

EXPERIMENTAL

$(\pi$-$C_5H_5)_2Ni$ was prepared in the usual way[3]. Benzene and n-hexane were purified and degassed before use.

IR spectra were recorded on a JASCO-IR-G spectrometer. Proton NMR spectra were recorded on a JEOL-JNM-4H100 NMR spectrometer with tetramethylsilane as the internal standard. Conductances were measured by the Wheatstone bridge method.

All experiments were conducted under dry nitrogen.

The reaction of nickelocene with allyl chloride in the presence of tri-n-butylphosphine

Allyl chloride (12 mmoles) was added to a stirred benzene solution of nickelocene (1 mmole) and tri-n-butylphosphine (3 mmoles) at room temperature under dry nitrogen. The colour changed immediately from green solution to red. The mixture was then refluxed for 2 h. The solvent was removed under vacuum to leave a reddish yellow residue. Extraction of the residue with n-hexane and recrystallization in the presence of tri-n-butylphosphine gave 0.54 g (95 % yield based on Ni) of green-yellow crystals, m.p. 85–87° (decompn.) (Found: C, 61.16; H, 10.59; Cl, 6.63; Ni, 9.98. $C_{29}H_{59}ClNiP_2$ calcd.: C, 61.81; H, 10.48; Cl, 6.31; Ni, 10.42 %.)

A similar reaction of allyl bromide (12 mmoles) with nickelocene (1 mmole) in the presence of tri-n-butylphosphine (3 mmoles) gave 0.60 g (98% yield based on Ni) of green-yellow crystals, m.p. 97–99° (decompn.). (Found: C, 56.90; H, 9.71; Ni, 9.41. $C_{29}H_{59}BrNiP_2$ calcd.: C, 57.20; H, 9.71; Ni, 9.66%.)

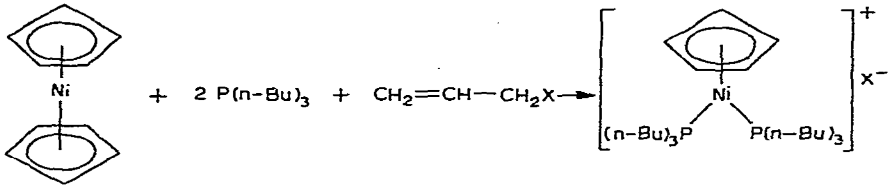
Similarly, reaction of allyl iodide (12 mmoles) with nickelocene (1 mmole) in the presence of tri-n-butylphosphine (3 mmoles) gave 0.59 g (90% yield based on Ni) of green-yellow crystals, m.p. 95–97° C (decompn.). (Found: C, 52.57; H, 9.14; Ni, 8.48. $C_{29}H_{59}INiP_2$ calcd.: C, 53.20; H, 9.01; Ni, 8.95%.)

RESULTS AND DISCUSSION

Nickelocene reacts with $CH_2{=}CH{-}CH_2Cl$ in the presence of $P(n\text{-}Bu)_3$ to give the green-yellow crystalline product of elementary formula $C_{29}H_{59}ClNiP_2$ (I). The IR spectrum of the solid resembles that of $\pi\text{-}C_5H_5Ni[P(n\text{-}Bu)_3]Cl$, and the proton NMR spectrum of the CS_2 solution shows bands at τ 7.5–9.3 (intensity 54) due to the $P(n\text{-}Bu)_3$ protons and a sharp singlet at τ 4.95 ppm (intensity 5) due to $\pi\text{-}C_5H_5$ protons. The compound is soluble in H_2O without decomposition, and its aqueous solution is a good conductor of electricity. These facts indicate that the product (I) is ionic, and it is formulated as $\{\pi\text{-}C_5H_5Ni[P(n\text{-}Bu)_3]_2\}^+Cl^-$.

The complexes $\{\pi\text{-}C_5H_5Ni[P(n\text{-}Bu)_3]_2\}^+Br^-$ (II) and $\{\pi\text{-}C_5H_5Ni[P(n\text{-}Bu)_3]_2\}^+I^-$ (III) were obtained analogously from $CH_2{=}CH{-}CH_2Br$ and $CH_2{=}CH{-}CH_2I$.

The proton NMR spectrum data and conductance data for the complexes (I), (II) and (III) are given in Table 1.



(X=Cl, Br, I)

TABLE 1

THE PROTON NMR DATA AND ELECTROLYTIC MOLAR CONDUCTANCE DATA FOR THE COMPLEXES (I)–(III)

Compound	Proton NMR data		Molar electrolytic conductance	
	$\tau[\pi\text{-}C_5H_5]$	$\tau[P(n\text{-}Bu)_3]$	Λ_m[a]	M
(I)	4.95	7.5~9.3	109.5	1.17×10^{-2}
(II)	4.90	7.5~9.3	110.0	3.50×10^{-3}
(III)	4.85	7.5~9.3	92.5	1.88×10^{-4}

[a] $Ohm^{-1}\cdot cm^2\cdot mole^{-1}$.

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