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

π-CYCLOPENTADIENYLS OF NICKEL(II)
IV*. *S*-BONDED ORGANONICKEL COMPOUNDS: *S*-SULFINATO- AND THIOLATO-NICKEL COMPOUNDS

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(Received June 29th, 1971)

SUMMARY

π-Cyclopentadienylbis(tri-n-butylphosphine)nickel chloride reacts with sodium benzenesulfinate and sodium *p*-toluenesulfinate in aqueous solution at room temperature to give π-cyclopentadienyl-*S*-(benzenesulfinato) (tri-n-butylphosphine)nickel, π-$C_5H_5Ni(PBu_3)SO_2Ph$ and π-cyclopentadienyl-*S*-(*p*-toluenesulfinato)(tri-n-butylphosphine)nickel, π-$C_5H_5Ni(PBu_3)SO_2C_6H_4CH_3$-*p*, respectively. It reacts similarly with sodium benzenethiolate and sodium α-toluenethiolate in aqueous solution at room temperature to give π-cyclopentadienyl(benzenethiolato)(tri-n-butylphosphine)nickel, π-$C_5H_5Ni(PBu_3)SPh$ and π-cyclopentadienyl(α-toluenethiolate)(tri-n-butylphosphine)nickel, π-$C_5H_5Ni(PBu_3)SCH_2Ph$, respectively.

π-$C_5H_5Ni(PBu_3)SH$ reacts with phenylacetylene to give π-$C_5H_5Ni(PBu_3)$-$SCPh{=}CH_2$, but with diphenylacetylene it gives $(\pi\text{-}C_5H_5)_2Ni_2(PhC{\equiv}CPh)$.

INTRODUCTION

It was recently observed that π-cyclopentadienylbis(tri-n-butylphosphine)nickel chloride reacts readily with various anions (X^-) in the aqueous solution to give ionic or covalent organonickel compounds[1,2].

$$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^- + X^- \rightarrow [\pi\text{-}C_5H_5Ni(PBu_3)_2]^+X^-$$
$$(X = NCO, NCS, N_3, ClO_4, ClO_3, NO_3 \text{ and } NO_2)$$
$$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+ Cl^- + X^- \rightarrow \pi\text{-}C_5H_5Ni(PBu_3)SH$$
$$(X = CN \text{ and } SH)$$

Though SH^- reacts with $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+ Cl^-$ to give π-$C_5H_5Ni(PBu_3)$-SH in good yield, OH^- does not give a corresponding organonickel compound, and we are thus interested in the bonding between nickel and sulfur. We now describe the reaction of sodium sulfinates and sodium thiolate with $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+ Cl^-$, and the reactions of π-$C_5H_5Ni(PBu_3)SH$ with acetylenes.

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* For part III, see ref. 2.

RESULTS AND DISCUSSION

$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ (I) and $C_6H_5SO_2Na$ reacted in aqueous solution to give green crystals which had the molecular formula $\pi\text{-}C_5H_5Ni(PBu_3)SO_2C_6H_5$ (II). Elementary analysis and proton NMR spectrum are consistent with the formula assigned. The IR spectrum between 1000 and 1200 cm^{-1} is similar to that reported for the *S*-bonded sulfinato compounds[3], and (II) was thus formulated as π-cyclopentadienyl-*S*-(benzenesulfinato)(tri-n-butylphosphine)nickel.

$$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+\,Cl^- + NaSO_2C_6H_5 \rightarrow \pi\text{-}C_5H_5Ni(PBu_3)SO_2C_6H_5 \quad \text{(II)}$$

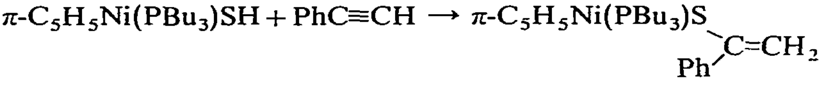
The reaction of (I) with $p\text{-}CH_3C_6H_4SO_2Na$ gave the green *S*-bonded sulfinato complex $\pi\text{-}C_5H_5Ni(PBu_3)SO_2C_6H_4CH_3\text{-}p$ (III).

Eliminations of SO_2 from *S*-sulfinato–metal complexes have been reported[4], but no thermal elimination occurred up to 150° with complexes (II) and (III).

The complex (I) reacted similarly with NaSPh and $NaSCH_2Ph$ in the aqueous solution to give $\pi\text{-}C_5H_5Ni(PBu_3)SPh$ (IV) and $\pi\text{-}C_5H_5Ni(PBu_3)SCH_2Ph$ (V), respectively.

The reaction of $\pi\text{-}C_5H_5Ni(PBu_3)SH$ *with phenylacetylene*

Phenylacetylene reacted with $\pi\text{-}C_5H_5Ni(PBu_3)SH$ in boiling benzene to give green crystals of the formula $\pi\text{-}C_5H_5Ni(PBu_3)SC_2H_2Ph$ (VI) in 17% yield (based on Ni). The IR spectrum of (VI) does not show the absorption near 2100 cm^{-1} characteristic of a C≡C stretching vibration. The proton NMR spectrum in CD_3COCD_3 showed multiplets centered at τ 2.7–2.8 ppm due to the phenyl protons (intensity 5), one sharp singlet at τ 4.65 ppm due to the π-cyclopentadienyl protons (intensity 5), complex multiplets at τ 8.2–9.3 ppm due to the protons of tri-n-butylphosphine (intensity 27) and a singlet at τ 3.35 ppm (intensity 2). There seems little doubt that the phenylacetylene has inserted into the S–H bond.



$$\pi\text{-}C_5H_5Ni(PBu_3)SH + PhC{\equiv}CH \rightarrow \pi\text{-}C_5H_5Ni(PBu_3)S\text{–}C(Ph){=}CH_2$$

(VI)

In contrast with the above results, treatment of diphenylacetylene with $\pi\text{-}C_5H_5\text{-}Ni(PBu_3)SH$ did not give the insertion product, but the complex $(\pi\text{-}C_5H_5)_2Ni_2\text{-}(PhC{\equiv}CPh)$[5], (VII), was obtained in 45% yield.

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

EXPERIMENTAL

$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+\,Cl^-$ and $\pi\text{-}C_5H_5Ni(PBu_3)SH$ were prepared as previously described[2]. Benzene, n-hexane, n-pentane 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-C-60-NMR spectrometer with tetramethylsilane as internal standard.

All experiments were conducted under dry nitrogen.

TABLE 1

SOME PROPERTIES OF THE NEW COMPLEXES

Complex	Colour	M.p. (°C)	Proton NMR spectra, τ values (ppm)			
			π-C_5H_5	PBu_3	Ph	Other
(II)	Green	116.5–117.5	5.18 (5)	8.1–9.2 (27)	2.5–2.8 (5)	
(IV)	Green	45–46	5.92 (5)	8.3–9.3 (27)	2.6–2.8 3.1–3.4 (5)	
(V)	Brown	31.5–32.0	4.84 (5)	8.3–9.3 (27)	2.8–2.9 (5)	CH_2 5.7 (2)
(VI)	Green	55–56	4.65 (5)	8.2–9.3 (27)	2.7–2.9 (5)	$=CH_2$ 3.35 (2)

The reaction of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+\ Cl^-$ *with* $NaSO_2Ph$

$NaSO_2Ph$ (3 mmoles) 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 green oil appeared immediately. The oil was taken up in 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 to give (II) as green crystals, m.p. 116.5–117.5°, in 95% yield. (Found: C, 58.52; H, 8.03; S, 6.70. $C_{23}H_{37}NiO_2PS$ calcd.: C, 59.13; H, 7.93; S, 6.85%.)

The reaction of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+\ Cl^-$ *with* $NaSO_2C_6H_4CH_3$-*p*

A similar procedure with 3 mmoles of $NaSO_2C_6H_4CH_3$-*p* and 1 mmole of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+\ Cl^-$ gave (III) as green crystals, m.p. 97.0–97.5°, in 98% yield. (Found: C, 59.85; H, 8.38; S, 6.52. $C_{24}H_{39}NiO_2PS$ calcd.: C, 59.93; H, 8.32; S, 6.64%.)

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

Similarly from the reaction with NaSPh (IV) was obtained as green crystals, m.p. 45.0–46.0° in 95% yield. (Found: C, 63.20; H, 7.62; mol.wt. cryoscopic in benzene 402. $C_{23}H_{37}NiPS$ calcd.: C, 63.49; H, 8.53%; mol.wt., 434.7.)

The reaction of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+\ Cl^-$ *with* $NaSCH_2Ph$

$NaSCH_2Ph$ (3 mmoles) 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 precipitate immediately appeared. The usual working-up gave (V) as brown crystals, m.p. 31.5–32.0°, 90% yield. (Found: C, 63.94; H, 9.34; S, 7.47; mol.wt. cryoscopic in benzene, 413. $C_{24}H_{39}NiPS$ calcd.: C, 64.18; H, 8.69; S, 7.15%; mol.wt., 449.)

The reaction of $\pi\text{-}C_5H_5Ni(PBu_3)SH$ *with* $PhC\equiv CH$

To 3 mmoles of $\pi\text{-}C_5H_5Ni(PBu_3)SH$ in 30 ml of benzene, was added 30 mmoles of $PhC\equiv CH$. The mixture was refluxed for 12 h. Chromatography on silica gel with 50% benzene/n-hexane as the eluant gave material which was recrystallized from n-hexane to give (VI) as green crystals, m.p. 55.0–56.0°, in 17% yield. (Found: C, 65.10; H, 8.55; S, 6.90. $C_{25}H_{39}NiPS$ calcd.: C, 65.11; H, 8.47; S. 6.95%.)

The reaction of π-$C_5H_5(NiPBu_3)SH$ *with* $PhC{\equiv}CPh$

To 3 mmoles of π-$C_5H_5Ni(PBu_3)SH$ in 30 ml of benzene was added 28 mmoles of $PhC{\equiv}CPh$. The mixture was warmed at 50° for 24 h, and the colour changed from brown to green. Working-up as in the preceding experiment gave (VII) as green crystals, m.p. 148.8–149.5°, (lit.[5] 149–150°) in 45% yield. (Found: C, 67.62; H, 4.70. $C_{24}H_{20}Ni_2$ calcd.: C, 67.70; H, 4.7%.)

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