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π-CYCLOPENTADIENYLS OF NICKEL(II)

VI. ALIPHATIC DITHIOL DIANION BRIDGED DINUCLEAR ORGANONICKEL COMPOUNDS

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SUMMARY

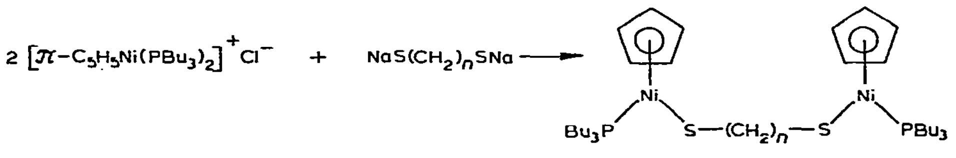
π-Cyclopentadienylbis(tri-n-butylphosphine)nickel chloride reacts with aliphatic dithiol dianions $[S-(CH_2)_n-S]^{2-}$ ($n=2$, 4 and 6) to give the dithiol dianion bridged dinuclear organonickel compounds, π-$C_5H_5(PBu_3)Ni-S(CH_2)_nS-Ni(PBu_3)$-$\pi$-$C_5H_5$.

INTRODUCTION

It has been shown previously that $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ reacts with NaSR ($R = Ph$ or CH_2Ph) in the aqueous solution to give π-$C_5H_5Ni(PBu_3)SR$ in good yield[1].

$$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^- + NaSR \rightarrow \pi\text{-}C_5H_5Ni(PBu_3)SR$$

The present study which deals with the reaction of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ with disodium aliphatic dithiolates, was undertaken with the aim of preparing dithiol dianion bridged organonickel compounds (I), and investigating their properties.



(I)

RESULTS AND DISCUSSION

When an ethanol solution of $NaS(CH_2)_2SNa$ is added to an aqueous solution of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ a reddish brown precipitate of the complex π-C_5H_5-$(PBu_3)NiS(CH_2)_2SNi(PBu_3)$-$\pi$-$C_5H_5$ (II) is produced. The IR spectrum of (II) resembles that of π-$C_5H_5Ni(PBu_3)SR$* ($R=$alkyl), and shows the characteristic out-of-plane deformation band of the π-cyclopentadienyl at 795 cm^{-1}. The proton NMR spectrum in C_6D_6 shows bands at τ 8.10–9.30 (intensity 54) due to the PBu_3 protons,

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* Unpublished work.

a sharp singlet at τ 4.75 (intensity 10) due to π-C_5H_5 protons, and a singlet at τ 7.50 (intensity 4) due to the $-S-(CH_2)_2-S-$ protons.

The green complexes, π-$C_5H_5(PBu_3)NiS(CH_2)_4SNi(PBu_3)$-$\pi$-$C_5H_5$ (III) and π-$C_5H_5(PBu_3)NiS(CH_2)_6SNi(PBu_3)$-$\pi$-$C_5H_5$ (IV), were obtained analogously from the reactions of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ with $NaS(CH_2)_4SNa$ and $NaS(CH_2)_6SNa$ respectively. The IR spectra of (III) and (IV) resemble each other; the characteristic out-of-plane deformation band of π-cyclopentadienyl appears at 790 cm^{-1} for the former and at 785 cm^{-1} for the latter. The proton NMR spectra of (III) and (IV) (Table 1) are consistent with the formulas; thus, the NMR spectrum of complex (III) in C_6D_6 shows a triplet at τ 7.80 due to the SCH_2 protons and a multiplet at τ 8.05 due to the $S-C-CH_2$ protons of the butane dithiol dianion, in addition to bands due to the π-C_5H_5 and PBu_3 protons, while complex (IV) shows a triplet at τ 7.85 due to the SCH_2 protons of the hexanedithiol dianion, though the other methylene protons are overlapped by the peaks of the PBu_3 protons.

TABLE 1

PROTON NMR DATA AND APPARENT MOLECULAR WEIGHTS FOR COMPLEXES (II), (III) AND (IV)

Compound	*Proton NMR data*[a]				*Mol.wt., found (calcd.)*
	$\tau(\pi\text{-}C_5H_5)$	$\tau(PBu_3)$	*Dithiol anion*		
(II)	4.75 (s)[b]	8.10–9.30	7.50 (s)		430
					(744)
(III)	4.77 (s)	8.20–9.30	7.80 (t)	$S-CH_2$	590
			8.05 (m)	$S-C-CH_2$	(772)
(IV)	4.77 (s)		7.85 (t)	$S-CH_2$	778
		8.00–9.3[c]			(800)

[a] In C_6D_6 solution, TMS as internal standard.
[b] s, singlet; t, triplet; m, multiplet.
[c] $\tau(PBu)_3 + \tau(-S-C-(CH_2)_4-C-S-)$.

The apparent molecular weights, determined by cryoscopy in benzene, of the complexes (II), (III) and (IV) (Table 1) are lower than the calculated values. Moreover, the benzene or hexane solutions of (II), (III) and (IV) are greenish brown, though solid (II) is reddish brown and solids (III) and (IV) are green. From these results, it was concluded that the complexes (II), (III), and (IV) dissociate in benzene or n-hexane. Since many thiolato metal compounds exist as dinuclear or polynuclear compounds, it seems reasonable that in these complexes it is the PBu_3 which dissociates.

EXPERIMENTAL

$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ was prepared as previously described[2]. The ethanol solution of disodium aliphatic dithiolate was prepared from Na and the aliphatic dithiol in ethanol[3]. Benzene, n-hexane, n-pentane, ethanol 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.

The reaction of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ *with* $NaS(CH_2)_2SNa$

$NaS(CH_2)_2SNa$ (2 mmoles) in 30 ml of ethanol was added to a solution of 1 mmole of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ in 50 ml of water at about 10°. A reddish brown precipitate appeared immediately. 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 (II) as reddish brown crystals, m.p. 70.0–71.0° (dec.), in 95% yield. (Found: C, 57.78; H, 9.69; S, 7.96. $C_{36}H_{68}Ni_2P_2S_2$ calcd.: C, 58.11; H, 9.15; S, 8.65%.)

The reaction of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ *with* $NaS(CH_2)_4SNa$

A similar procedure with 1 mmole of $NaS(CH_2)_4SNa$ and 1 mmole of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ gave (III) as green crystals, m.p. 101–102°, in 70% yield. (Found: C, 58.20; H, 9.47; S, 8.38. $C_{38}H_{72}Ni_2P_2S_2$ calcd.: C, 59.11; H, 9.33; S, 8.30%.)

The reaction of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ *with* $NaS(CH_2)_6SNa$

Similarly from the reaction with $NaS(CH_2)_6SNa$, (IV) was obtained as green crystals, m.p. 85.0–87.0°, in 75% yield. (Found: C, 59.25; H, 9.60; S, 8.32. $C_{40}H_{76}Ni_2P_2S_2$ calcd.: C, 60.04; H, 9.51; S, 8.01%.)

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