Journal of Organometallic Chemistry, 70 (1974) 101—106

π-CYCLOPENTADIENYLS OF NICKEL(II)

XIV. PREPARATION AND PROPERTIES OF ORGANONICKEL DERIVATIVES OF 1-SUBSTITUTED TETRAZOLINE 5-THIONES

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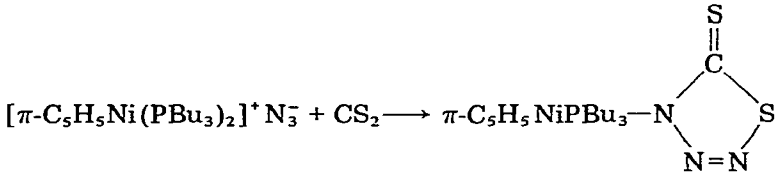
(Received September 14th, 1973)

Summary

The *N*-bonded tetrazoline-5-thione organonickel compounds π-$C_5H_5NiPBu_3$-N_4CSR(III) ($R = C_6H_5$, CH_3 and C_2H_5), have been prepared from the reaction between π-$C_5H_5NiPBu_3N_3$ and RNCS and /or from the reaction of [π-C_5H_5Ni-$(PBu_3)_2$]$^+Cl^-$ with NaN_4CSR. The compound III reacts with PBu_3 to give the ionic compound [π-$C_5H_5Ni(PBu_3)_2$]$^+$$(N_4CSR)^-$ (IV), which reversibly dissociates to the reactants in non-polar solvents.

Introduction

Recently a number of cycloadditions of dipolarophiles such as CS_2 and RNCS to the coordinated azide group of inorganic compounds have been described [1]. Thus, we prepared π-cyclopentadienylbis(tributylphosphine)nickel azide [2], [π-$C_5H_5Ni(PBu_3)_2$]$^+N_3^-$, (I), and found that it reacted with CS_2 to give the *N*-bonded thiatriazole organonickel compound II [3].



(I) (II)

We report below the reaction of I with RNCS and the properties of the new *N*-bonded tetrazoline-5-thione compounds (III) thus obtained.

Results and discussion

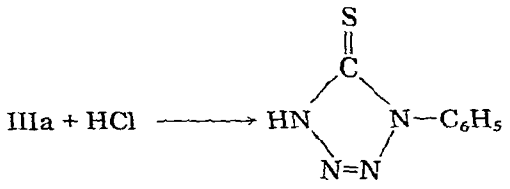
Reaction of π-$C_5H_5NiPBu_3N_3$ with RNCS (R = C_6H_5, CH_3 and C_2H_5)

A benzene solution of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+N_3^-$* (I) and C_6H_5NCS was allowed to stand for a few hours at room temperature, the benzene was then evaporated off under vacuum and the resulting brownish-green residue was chromatographed on silica gel. Hexane elution gave PBu_3, C_6H_5NCS and π-$C_5H_5NiPBu_3$-NCS, and with ether elution red crystals of π-$C_5H_5NiPBu_3N_4CSC_6H_5$ (IIIa) were obtained. Recrystallization of IIIa from hexane in the presence of PBu_3 gave the green ionic compound $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+(N_4CSC_6H_5)^-$ (IVa). The colour of the methyl alcohol or ethyl alcohol solution of IVa was brownish-green, but the solution of IVa in a non-polar solvent was red. From the above results, together with the NMR data described below, it was deduced that IVa dissociated in non-polar solvents according to eqn. 2. Thus the brownish-green residue obtained from the reaction between $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+N_3^-$ and C_6H_5NCS must be a mixture of IVa with other by-products.

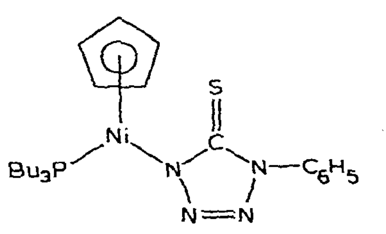
$$\underset{\text{(I)}}{[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+N_3^-} + C_6H_5NCS \longrightarrow \underset{\text{(IVa)}}{[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+(N_4CSC_6H_5)^-} \qquad (1)$$

$$\underset{\text{(IVa)}}{[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+(C_6H_5N_4CS)^-} \underset{PBu_3}{\overset{\text{non polar solvent}}{\rightleftharpoons}} \underset{\text{(IIIa)}}{\pi\text{-}C_5H_5NiPBu_3N_4CSC_6H_5} + PBu_3 \qquad (2)$$

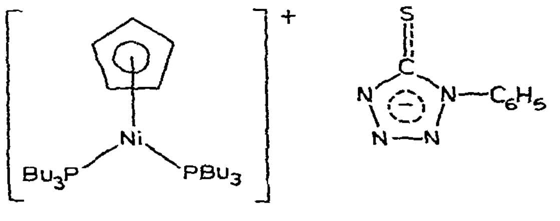
IIIa reacted with aqueous HCl in methyl alcohol** to give 1-phenyl-tetrazoline-5-thione [4].



From the above result and the IR and NMR spectra, we formulate IIIa and IVa as shown below.



(IIIa)



(IVa)

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* $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+N_3^-$ dissociates into π-$C_5H_5NiPBu_3N_3$ and PBu_3 in benzene solution [2].

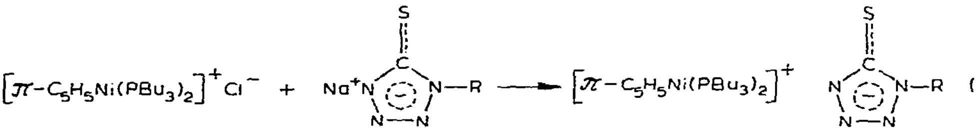
** Without excess PBu_3, IIIa exists as a covalent complex in methyl alcohol.

Compound IIIa was stable and π-$C_5H_5NiPBu_3NCS$ was not obtained by pyrolysis of IIIa although π-$C_5H_5NiPBu_3N_3CS_2$ (II) gave π-$C_5H_5NiPBu_3NCS$ on pyrolysis. Therefore the π-$C_5H_5NiPBu_3NCS$ which was obtained by the reaction of I with C_6H_5NCS was not a decomposition product of IIIa, but must have been obtained by another route. Similarly, we investigated the reaction of I with CH_3NCS and C_2H_5NCS. The colour of the benzene solution of I and CH_3NCS (or C_2H_5NCS) on standing at room temperature changed from red to brown, but from this brown solution we could not isolate any nickel-containing products such as π-$C_5H_5NiPBu_3NCS$ or π-$C_5H_5NiPBu_3N_4CSR$.

Reaction of [π-$C_5H_5Ni(PBu_3)_2$]$^+Cl^-$ with $Na^+(N_4CSR)^-$ ($R = C_6H_5$, CH_3 and C_2H_5)

Many complexes of the type π-$C_5H_5NiPBu_3X$ (X = anion) have been obtained from reactions between [π-$C_5H_5Ni(PBu_3)_2$]$^+$ Cl^- and NaX in aqueous solution [2], so we investigated the reaction of [π-$C_5H_5Ni(PBu_3)_2$]$^+Cl^-$ with $Na^+(N_4CSR)^-$ as a source of a type III compound.

When an aqueous solution of [π-$C_5H_5Ni(PBu_3)_2$]$^+Cl^-$ was treated at room temperature with an excess of aqueous $NaN_4CSC_6H_5$, an instantaneous reaction occurred and the green compound IVa was formed in excellent yield (eqn. 3).



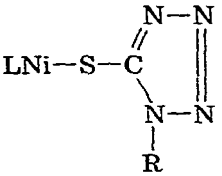
(3)

$R = C_6H_5$ (IVa), CH_3 (IVb), C_2H_5 (IVc).

Chromatography of IVa on silica gel using n-hexane as the eluant gave PBu_3 and with ether as eluant gave IIIa. Similar reactions occur with $R = CH_3$ and C_2H_5, giving green IVb and IVc, which are converted to red compounds IIIb ($R = CH_3$) and IIIc ($R = C_2H_5$), respectively, by similar treatment on silica gel. IIIb and IIIc reacted with aqueous HCl in methyl alcohol to give the corresponding 1-substituted tetrazoline-5-thiones.

IR spectra

Lieber et al. have studied the IR spectra of 1-substituted tetrazoline-5-thiones and reported that, in all compounds studied, the N—C=S and C=S absorptions are strong and appeared in the regions 1500—1474 cm^{-1} and 1359—1338 cm^{-1}, respectively [4]. Agarwale et al. have reported that the characteristic band in the region 1500—1474 cm^{-1} disappeared when 1-substituted tetrazoline-5-thiones were bonded to transition metals [5]. IIIa shows an N—C=S band at 1498 cm^{-1} and a C=S band at 1370 cm^{-1}, but IIIb and IIIc have no absorption in the region 1500—1474 cm^{-1}, although they do have C=S bands at 1358 cm^{-1} and 1375 cm^{-1}, respectively. It has been shown that 1-substituted tetrazoline-5-thiones exist in the thione form alone [4], but there is the possibility of tautomerism to the thiol form during reaction. Thus there is the possibility that the complexes are formed by replacing the proton of the thiol group with a metal ion as in:



(A) (L = π-$C_5H_5\cdot PBu_3$).

However, the IR spectrum of IIIa shows the characteristic band for N—C=S and all known transition metal compounds are of the thione type, so we have formulated III as a thione-type complex.

NMR spectra

The proton NMR spectrum of IIIa in CD_3OD shows bands at τ 2.2—2.6 due to phenyl protons, a singlet at τ 4.72 due to π-C_5H_5 protons and bands at τ 8.1—9.3 due to PBu_3 protons; that of IVa in CD_3OD shows bands at τ 1.90—2.20, τ 2.3—2.7 due to phenyl protons, a singlet at τ 4.48 due to π-C_5H_5 protons and bands at τ 7.90—8.30 due to PBu_3 protons. The appearance of the π-C_5H_5 protons of IVa at lower magnetic fields than those of IIIa, was also found in IVb compared to IIIb and IVc compared to IIIc. These results indicate that the carbon atoms of π-C_5H_5 in IV have more *s* character than those of III, or, alternatively, that larger diamagnetic circulation of the π-electron system is induced in π-C_5H_5 for IV than for III. The degree of dissociation of IVc to [IIIc + PBu_3] in CD_3OD or CS_2 has been investigated using NMR spectra. IVc in CD_3OD shows a singlet at τ 4.44 (due to π-C_5H_5) and a very small peak at τ 4.68, while IIIc in CD_3OD shows a singlet at τ 4.68 (due to π-C_5H_5) and no peak at τ 4.44. This indicates that IVc does not dissociate in CD_3OD. Moreover, this conclusion is supported by the fact that when excess (about 5-fold mole excess) of PBu_3 was added to IIIc in CD_3OD, the π-C_5H_5 protons appeared at τ 4.44 and no peak was found at τ 4.68, but when 1/2 mole of PBu_3 was added to 1 mole of IIIc in CD_3OD, the π-C_5H_5 protons appeared at τ 4.44 and at τ 4.68 with about equal intensity. It was found that IVc is dissociated completely to [IIIc and PBu_3] in CS_2 and even when excess PBu_3 (about 5-fold excess) was added to IIIc only one peak due to π-C_5H_5 appeared at τ 4.80.

NMR results are summarized in Table 1.

Experimental

[π-$C_5H_5Ni(PBu_3)_2$]$^+Cl^-$ and [π-$C_5H_5Ni(PBu_3)_2$]$^+N_3^-$ were prepared as previously described [2]. The aqueous solution of NaN_4CSR was prepared from isothiocyanate and NaN_3 [4]. The IR and NMR spectra were recorded with JASCO IR-G and JEOL JNM 4H-100-NMR spectrometers, respectively.

Reaction of [π-$C_5H_5Ni(PBu_3)_2$]$^+N_3^-$ with PhNCS

PhNCS (3 mmoles) was added to a solution of 2 mmoles of [π-$C_5H_5Ni(PBu_3)_2$]$^+N_3^-$ in 30 ml of benzene. After the mixture had been allowed to stand for 3h at room temperature, the solvent was evaporated under vacuum. Chromatography on silica gel with n-hexane as eluant gave unreacted PhNCS and 0.11 g of π-$C_5H_5NiPBu_3NCS$ (14% yield based on Ni), and with ether as eluant

TABLE 1

PROTON NMR SPECTRA OF III AND IV[a]

Compound	CD_3OD solvent			CS_2 solvent		
	(π-C_5H_5)	(PBu_3)	other	(π-C_5H_5)	(PBu_3)	other
III.	4.72 s	8.1—9.3	2.2—2.6 (C_6H_5)	4.85 s	8.4—9.4	2.2—2.9 (C_6H_5)
IVa	4.48 s	7.9—9.3	1.9—2.2 2.3—2.7 (C_6H_5)			
IIIb	4.72 s	8.2—9.3	6.18 s (CH_3)	4.82 s	8.2—9.3	6.37 s (CH_3)
IVb	4.44 s	7.9—9.3	6.18 s (CH_3)			
IIIc	4.68 s	8.0—9.3[b]	5.68 q (CH_2)	4.80 s	8.0—9.3	5.93 q (CH_2) 8.70 t ($C-CH_3$)
IVc	4.44 s	7.9—9.3[b]	5.71 q (CH_2)			
IIIc + $\frac{1}{2}PBu_3$	4.44 s 4.68 s	8.1—9.3[b]	5.68 q (CH_2) 5.71 q (CH_2)			
IIIc + $5PBu_3$	4.44 s	7.9—9.3[b]	5.71 q (CH_2)	4.80 s	8.0—9.3	5.93 q (CH_2) 8.70 t ($C-CH_3$)

[a] TMS as internal standard, values in ppm on τ scale. s=singlet, t=triplet, q=quartet. [b] (PBu_3) + ($C-CH_3$).

gave a red product which was recrystallized from ether—hexane mixture to give 0.18 g of IIIa (18% yield) m.p. 69—70°C. (Found: C, 56.87; H, 7.21; N, 11.05. $C_{24}H_{37}N_4NiPS$ calcd.: C, 57.26; H, 7.36; N, 11.13%.)

Reaction of [π-$C_5H_5Ni(PBu_3)_2$]$^+Cl^-$ with NaN_4CSPh

Excess of NaN_4CSPh in water was added to a solution of 2 mmoles of [π-$C_5H_5Ni(PBu_3)_2$]$^+Cl^-$ in 50 ml of water at room temperature. A green precipitate appeared immediately. Recrystallization of this precipitate from a benzene—hexane mixture in the presence of PBu_3 gave 1.2 g of IVa (85% yield) as green crystals, m.p. 74.0—74.5°C. (Found: C, 60.45; H, 9.25; N, 7.85. $C_{36}H_{64}N_4NiP_2S$ calcd.: C, 61.28; H, 9.08; N, 7.94%.)

Reaction of [π-$C_5H_5Ni(PBu_3)_2$]$^+Cl^-$ with NaN_4CSCH_3

A similar procedure, using excess NaN_4CSCH_3 and 2 mmoles of [π-C_5H_5-$Ni(PBu_3)_2$]$^+Cl^-$, gave IVb as green crystals in 91% yield, m.p. 57—58°C. (Found: C,57.42; H,9.90; N,8.43. $C_{31}H_{62}N_4NiP_2S$ calcd.: C, 57.85; H, 9.64; N, 8.71%.)

Reaction of [π-$C_5H_5Ni(PBu_3)_2$]$^+Cl^-$ with $NaN_4CSC_2H_5$

Similarly, excess $NaN_4CSC_2H_5$ with 2 mmoles of [π-$C_5H_5Ni(PBu_3)_2$]$^+Cl^-$ gave IVc as green crystals in 88% yield, m.p. 49—50°C. (Found: C, 57.79; H, 10.02; N,8.15. $C_{32}H_{64}N_4NiP_2S$ calcd.: C, 58.45; H, 9.74; N, 8.52%.)

Preparation of IIIa from IVa

Chromatography on silica gel of IVa with n-hexane as the eluant gave PBu_3, and with ether as the eluant gave IIIa in 65% yield.

Preparation of IIIb from IVb

Similar treatment of IVb on silica gel, gave IIIb in 60% yield, m.p. 54.5—55°C. (Found: C,51.32; H,8.30; N,12.82. $C_{19}H_{35}N_4NiPS$ calcd.: C,51.70; H,7.94; N,12.70%.)

Preparation of IIIc from IVc

Similar treatment of IVc on silica gel, gave IIIc in 60% yield, m.p. 69—70°C. (Found: C, 52.66; H, 8.41; N, 12.36. $C_{20}H_{37}N_4NiPS$ calcd.: C, 52.75; H, 8.13; N, 12.31%.)

Reaction of IIIa with HCl in methanol

5 ml of 34% aqueous HCl solution was added to 0.6 g (1.18 mmoles) of IIIa in 10 ml of methanol at room temperature. An instantaneous reaction occurred and the red solution turned green. After removal of solvent under vacuum, the resulting residue was dissolved in 30 ml of ether and this ether solution was then washed three times with 30 ml of water. After drying over anhydrous calcium chloride, the ether was removed under vacuum to leave a white residue. Recrystallization from ether—n-hexane gave 0.20 g (94% yield) of 1-phenyl tetrazoline-5-thione, m.p. 149°C (lit. [4] 150°). (Found: C, 47.01; H, 3.81; N, 30.81. $C_7H_6N_4S$ calcd.: C, 47.19; H, 3.37; N, 31.46%.)

Reaction of IIIb with HCl in methanol

Similarly 0.8 g (1.81 mmoles) of IIIb and excess HCl gave 0.19 g (90.6% yield) of 1-methyl tetrazoline-5-thione, m.p. 125°C (lit. [4] 125—126°). (Found: C,20.10; H,3.81; N,49.12. $C_2H_4N_4S$ calcd.: 20.68; H, 3.47; N, 48.24%.)

Reaction of IIIc with HCl in methanol

0.52 g (1.14 mmoles) of IIIc and excess HCl gave 0.13 g (88% yield) of 1-ethyl tetrazoline-5-thione, m.p. 49.0—49.5°C (lit. [4] 50°). (Found: C, 27.38; H,4.45; N,43.00. $C_3H_6N_4S$ calcd.: C, 27.68; H, 4.65; N, 43.04%.)

References

1 (a) W. Beck, W.P. Fehlhammer, Angew. Chem., 79 (1967) 146.
  (b) P. Kreutzer, C.W.H. Boehme, T. Kemmerich, W. Beck, C. Spencer and R. Mason, Z. Naturforsch., 27b (1972) 415.
2 M. Sato, F. Sato and T. Yoshida, J. Organometal. Chem., 31 (1971) 415.
3 F. Sato, M. Etoh and M. Sato, J. Organometal. Chem., 37 (1972) C51.
4 (a) E. Lieber and J. Ramachandran, Can. J. Chem., 37 (1959) 101.
  (b) E. Lieber, C.N.R. Rao, C.N. Piliai, J. Ramachandran and R.D. Hites, ibid, 36 (1958) 801.
5 U. Agarwala, V.A. Narayan and S.K. Dikshit, Can. J. Chem., 45 (1967) 1057.