

## $\pi$ -CYCLOPENTADIENYLS OF NICKEL(II)

### XV \*. INSERTION REACTION OF RNCS INTO THE NICKEL—CARBON BOND

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#### Summary

$\eta^5$ -C<sub>5</sub>H<sub>5</sub>NiPBu<sub>3</sub>CH(CN)<sub>2</sub> (I) readily undergoes ethyl- or phenyl-isothiocyanate insertion, producing the stable products  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>NiPBu<sub>3</sub>SC(NRH) = C(CN)<sub>2</sub> (IIIa; R = C<sub>2</sub>H<sub>5</sub>, IIIb; R = C<sub>6</sub>H<sub>5</sub>).  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>NiPh<sub>3</sub>CH(CN)<sub>2</sub> (II) reacts with RNCS (R = C<sub>2</sub>H<sub>5</sub> and C<sub>6</sub>H<sub>5</sub>) to undergo two types of insertion reaction; with C<sub>2</sub>H<sub>5</sub>NCS,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>NiPh<sub>3</sub>SC[N(C<sub>2</sub>H<sub>5</sub>)H] = C(CN)<sub>2</sub> (IVa) is obtained, with C<sub>6</sub>H<sub>5</sub>NCS, on the other hand,  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>NiPh<sub>3</sub>SC(=NC<sub>6</sub>H<sub>5</sub>)CH(CN)<sub>2</sub> (IVb) is produced.

IIIa and IIIb react with PBu<sub>3</sub> to give ionic complexes  $[\eta^5$ -C<sub>5</sub>H<sub>5</sub>Ni(PBu<sub>3</sub>)<sub>2</sub>]<sup>+</sup>[SC(NC<sub>2</sub>H<sub>5</sub>H)=C(CN)<sub>2</sub>]<sup>-</sup> (Va) and  $[\eta^5$ -C<sub>5</sub>H<sub>5</sub>Ni(PBu<sub>3</sub>)<sub>2</sub>]<sup>+</sup>[SC(=NC<sub>6</sub>H<sub>5</sub>)CH(CN)<sub>2</sub>]<sup>-</sup> (Vb), respectively.

#### Introduction

The insertion reactions of CS<sub>2</sub> or RNCS into transition metal—carbon bonds have received much attention [1]. Although many insertion reactions of CS<sub>2</sub> have been reported, only a few cases of RNCS insertions are known [2]. Recently we have investigated the reactivity of compounds of the type  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>NiPBu<sub>3</sub>X. It has been shown that  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>NiPBu<sub>3</sub>SR compounds readily undergo CS<sub>2</sub> insertion to produce the stable compound  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>NiPBu<sub>3</sub>SC(S)SR [3] and that  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>-NiPBu<sub>3</sub>SC<sub>2</sub>H<sub>5</sub> also undergoes C<sub>6</sub>H<sub>5</sub>NCS insertion to give  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>NiPBu<sub>3</sub>[SC(=NC<sub>6</sub>H<sub>5</sub>)SC<sub>2</sub>H<sub>5</sub>] [4]. This paper describes the insertion reactions of RNCS (R = C<sub>2</sub>H<sub>5</sub> and C<sub>6</sub>H<sub>5</sub>) with  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>NiPR'<sub>3</sub>CH(CN)<sub>2</sub> (R' = Bu and Ph), and some properties of the compounds thus obtained.

\* For part XIV see ref. 8.

## Results and discussion

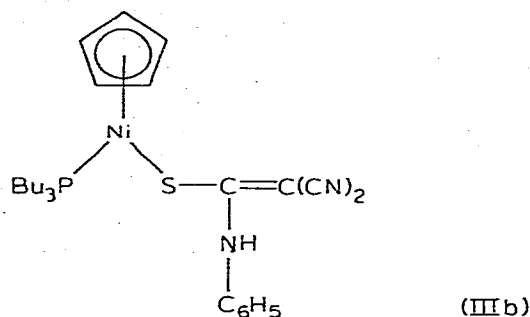
### Preparation of $\eta^5\text{-C}_5\text{H}_5\text{NiPR}_3\text{CH}(\text{CN})_2$ ( $R = \text{Bu}$ and $\text{Ph}$ )

A large number of phosphine-stabilized  $\pi$ -cyclopentadienyl-alkyls and -aryls have been prepared by the reaction of a  $\pi$ -cyclopentadienylnickel halide with Grignard or organolithium reagents [5].

$\pi$ -cyclopentadienyltri-*n*-butylphosphinenickel malononitrile,  $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{CH}(\text{CN})_2$  (I), and  $\pi$ -cyclopentadienyltriphenylphosphinenickel malononitrile,  $\eta^5\text{-C}_5\text{H}_5\text{NiPPh}_3\text{CH}(\text{CN})_2$  (II), were obtained from reactions of  $\eta^5\text{-C}_5\text{H}_5\text{NiPBu}_3\text{Cl}$  and  $\eta^5\text{-C}_5\text{H}_5\text{NiPPh}_3\text{Cl}$  with sodium malononitrile, respectively, in excellent yield.

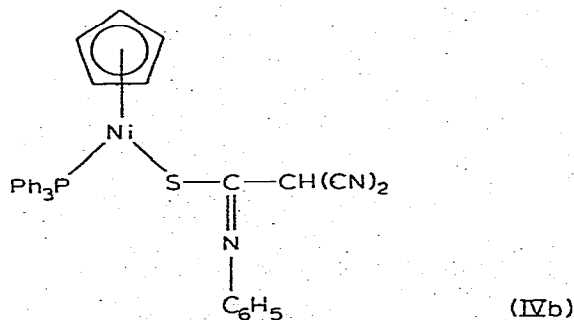
### Reactions of RNCS with I and II

After standing for 24 h at room temperature, a mixture of an excess of  $\text{C}_6\text{H}_5\text{NCS}$  and I in benzene gave reddish-brown crystals which had the molecular formula  $\eta^5\text{-C}_5\text{H}_5\text{NiPBu}_3\text{CH}(\text{CN})_2\text{C}_6\text{H}_5\text{NCS}$ . Based on its IR and NMR spectra, the product was formulated as:



The IR spectrum of IIIb showed absorption bands at 3210 [ $\nu(\text{NH})$ ] and 2180  $\text{cm}^{-1}$  [ $\nu(\text{C}\equiv\text{N})$ ]. The  $^1\text{H}$  NMR peaks of IIIb in  $\text{CDCl}_3$  appeared at  $\tau$  8.3–9.2 ( $\text{PBu}_3$ , 27H), 4.71 ( $\eta^5\text{-C}_5\text{H}_5$ , s, 5H), 2.5–2.9 (aromatic, 5H) and 1.82 ppm (NH, broad, 1H). IIIb was also obtained by reaction between  $\eta^5\text{-C}_5\text{H}_5\text{NiPBu}_3\text{Cl}$  and  $\text{NaSC}(\text{NHC}_6\text{H}_5)=\text{C}(\text{CN})_2$  [6].

A similar reaction of II with  $\text{C}_6\text{H}_5\text{NCS}$  gave red crystals which had the molecular formula  $\eta^5\text{-C}_5\text{H}_5\text{NiPPh}_3\text{CH}(\text{CN})_2\text{C}_6\text{H}_5\text{NCS}$  (IVb). Surprisingly, the IR spectrum of IVb showed no  $\nu(\text{NH})$ , and the  $^1\text{H}$  NMR spectrum showed no peak due to an NH proton but a singlet at  $\tau$  8.44 ppm due to the CH proton of  $\text{CH}(\text{CN})_2$ . In addition to the peaks which are assigned to the phenyl and  $\eta^5\text{-C}_5\text{H}_5$  protons. Thus we formulated IVb as shown below:



IVb was also obtained by reaction of  $\eta^5\text{-C}_5\text{H}_5\text{NiPPh}_3\text{Cl}$  and  $\text{NaS-C(NHC}_6\text{H}_5\text{)=C(CN)}_2$ .

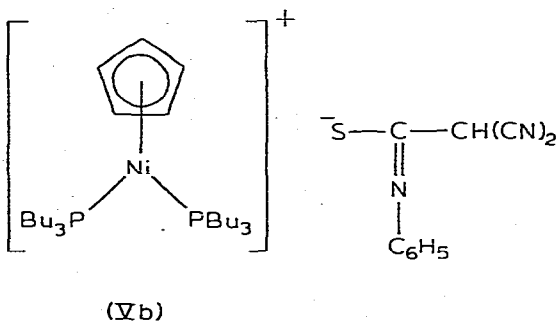
$\text{C}_2\text{H}_5\text{NCS}$  also inserted into the nickel-carbon bond of I and II to afford  $\eta^5\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SC(NHC}_2\text{H}_5\text{)=C(CN)}_2$  (IIIa) and  $\eta^5\text{-C}_5\text{H}_5\text{NiPPh}_3\text{SC(NHC}_2\text{H}_5\text{)=C(CN)}_2$  (IVa), respectively. The properties and elemental analysis data of compounds IIIa, IIIb and IVa, IVb are given in Table 1. In Table 2 the IR and NMR data are listed.

It is interesting to find that the mode of insertion of RNCS into  $\eta^5\text{-C}_5\text{H}_5\text{NiPR}'_3\text{-CH(CN)}_2$  is dependent on R and R', but it is not clear why such differences exist.

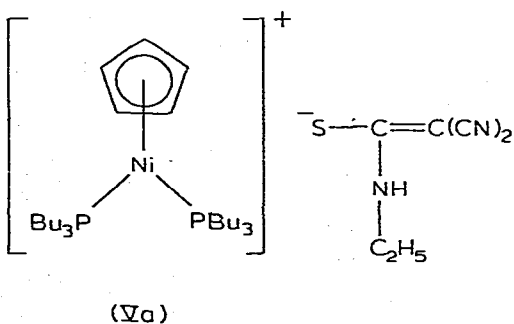
#### Reaction of IIIa and IIIb with $\text{PBu}_3$

Many complexes of the type  $[\eta^5\text{-C}_5\text{H}_5\text{Ni(PBu}_3\text{)}_2]\text{X}$  (X = anion) have been obtained from reactions between  $\eta^5\text{-C}_5\text{H}_5\text{NiPBu}_3\text{X}$  and  $\text{PBu}_3$  [7], so we investigated the reaction of IIIa and IIIb with  $\text{PBu}_3$ .

A  $\text{CH}_2\text{Cl}_2$  solution of IIIb was treated with an equimolar amount of  $\text{PBu}_3$ , and an instantaneous reaction occurred, the green compound Vb was formed in excellent yield. The IR and NMR spectra (Table 2) indicated that Vb can be formulated as shown below:



In contrast with the above result, the product obtained from a similar reaction of IIIa with  $\text{PBu}_3$  was formulated based on IR and NMR data (Table 2).



### Experimental

$\text{NaS-C(NHC}_6\text{H}_5\text{)=C(CN)}_2$  was prepared by the method described in the literature [6]. IR spectra were recorded on a JASCO-IR-G spectrometer. Proton NMR

TABLE 1  
SOME PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR COMPOUNDS III, IV AND V

Compound	Color	M.p. (°C)	Analyses: found (calcd.), %			
			C	H	N	S
$\eta^5\text{-C}_5\text{H}_5\text{Ni}(\text{PBu}_3)\text{SC}(\text{NHC}_2\text{H}_5)=\text{C}(\text{CN})_2$ (IIIa)	Red	76-77	58.0 (57.8)	7.9 (8.0)	8.8 (8.8)	6.6 (6.7)
$\eta^5\text{-C}_5\text{H}_5\text{Ni}(\text{PBu}_3)\text{SC}(\text{NHC}_6\text{H}_5)=\text{C}(\text{CN})_2$ (IIIb)	Reddish brown	115-116	61.6 (61.6)	7.6 (7.2)	8.1 (8.0)	6.1 (6.1)
$\eta^5\text{-C}_5\text{H}_5\text{Ni}(\text{PPh}_3)\text{SC}(\text{NHC}_2\text{H}_5)=\text{C}(\text{CN})_2$ (IVa)	Red	150-151.5	64.4 (64.7)	4.8 (4.9)	7.6 (7.8)	5.9 (6.0)
$\eta^5\text{-C}_5\text{H}_5\text{Ni}(\text{PPh}_3)\text{SC}(\text{=NC}_6\text{H}_5)\text{CH}(\text{CN})_2$ (IVb)	Red	173.5-175	68.0 (67.6)	4.2 (4.4)	6.8 (7.2)	5.8 (5.5)
$[\eta^5\text{-C}_5\text{H}_5\text{Ni}(\text{PBu}_3)_2]^+[\text{SC}(\text{NHC}_2\text{H}_5)=\text{C}(\text{CN})_2]^-$ (Va)	Green	88-89	61.6 (61.8)	9.3 (9.6)	6.2 (6.2)	4.4 (4.7)
$[\eta^5\text{-C}_5\text{H}_5\text{Ni}(\text{PBu}_3)_2]^+[\text{SC}(\text{=NC}_6\text{H}_5)\text{CH}(\text{CN})_2]^-$ (Vb)	Green	35-37	64.4 (64.3)	9.2 (9.0)	5.4 (5.8)	4.3 (4.4)

TABLE 2

 $^1\text{H}$  NMR AND IR DATA FOR COMPOUNDS III, IV AND V

Compound	$^1\text{H}$ NMR data <sup>a</sup> ( $\tau$ , ppm)				IR data <sup>b</sup> ( $\text{cm}^{-1}$ )	
	$\eta^5\text{-C}_5\text{H}_5$	NH	PBu <sub>3</sub>	Other	$\nu(\text{NH})$	
IIIa	4.75 s <sup>c</sup>	3.48(br)	8.3-9.2 <sup>d</sup>	6.34(p) <sup>f</sup> (N-CH <sub>2</sub> )	3200	
IIIb	4.71 s	1.82(br)	8.3-9.2	2.5-2.9	3210	
IVa	4.79 s	3.71(br)		2.2-2.8	3230	
IVb	4.79 s			2.2-3.2	—	
Va	4.56 s	3.89(br)	8.2-9.2 <sup>d</sup>	8.91(t) (N-C-CH <sub>3</sub> ) 8.44(s) [CH(CN) <sub>2</sub> ]	—	
Vb	4.59 s		8.3-9.2 <sup>e</sup>	6.33(p) (N-CH <sub>2</sub> ) 2.1-3.0	3270	

<sup>a</sup> Measured in CDCl<sub>3</sub>. <sup>b</sup> KBr. <sup>c</sup>s, strong; (br) broad, <sup>d</sup> PBu<sub>3</sub> + N-C-OH<sub>3</sub>, <sup>e</sup> PBu<sub>3</sub> + CH(CN)<sub>2</sub>. <sup>f</sup>s, singlet; t, triplet; p, pentaplet.

spectra were recorded on a JEOL-JNM-4H 100NMR spectrometer with TMS as the internal standard.

*Reaction of  $\eta^5\text{-C}_5\text{H}_5\text{NiPBu}_3\text{Cl}$  with  $\text{NaCH}(\text{CN})_2$*

When 0.26 g (3 mmol) of  $\text{NaCH}(\text{CN})_2$  was added to a 20 ml of ether solution of  $\eta^5\text{-C}_5\text{H}_5\text{NiPBu}_3\text{Cl}$  (0.36 g, 1 mmol) at room temperature, the color of the solution changed from red to green-brown. After 3 h stirring, the solvent was removed and the residue was crystallized from ether/n-hexane to give 0.33 g (84% yield) of I: m.p. 79.5–80°C; NMR  $\tau$  5.04 (s,  $\eta^5\text{-C}_5\text{H}_5$ ) and 8.6–9.4 ppm [ $\text{PBu}_3 + \text{CH}(\text{CN})_2$ ] (measured in  $\text{CDCl}_3$ ). Anal. Found: C, 60.9; H, 8.6; N, 7.1.  $\text{C}_{20}\text{H}_{33}\text{N}_2\text{NiP}$  calcd.: C, 61.4; H, 8.4; N, 7.2%.

*Reaction of  $\eta^5\text{-C}_5\text{H}_5\text{NiPPh}_3\text{Cl}$  with  $\text{NaCH}(\text{CN})_2$*

$\text{NaCH}(\text{CN})_2$  (0.26 g, 3 mmol) was added to a solution of 0.42 g (1 mmol) of  $\eta^5\text{-C}_5\text{H}_5\text{NiPPh}_3\text{Cl}$  in 20 ml of benzene, the mixture was then stirred for 3 h at room temperature. The solvent was removed under vacuum and the residue crystallized from benzene/n-hexane to give 0.32 g (70% yield) of II: m.p. 147.5–148.5°C; NMR  $\tau$  4.78 (s,  $\eta^5\text{-C}_5\text{H}_5$ ), 2.2–2.8 ( $\text{PPh}_3$ ) and 9.10 ppm [ $\text{d,CH}(\text{CN})_2$ ,  $J(\text{P-CH})$  12.2 Hz] (measured in  $\text{CDCl}_3$ ). Anal. Found: C, 68.9; H, 4.5; N, 6.1.  $\text{C}_{26}\text{H}_{21}\text{N}_2\text{NiP}$  calcd.: C, 69.2; H, 4.8; N, 6.2%.

*Reaction of I with  $\text{C}_6\text{H}_5\text{NCS}$*

A solution containing I (0.39 g, 1 mmol) and  $\text{C}_6\text{H}_5\text{NCS}$  (5 g, 40 mmol) in 20 ml benzene was stirred at room temperature for 24 h. The solution was evaporated to dryness and the residue was crystallized from  $\text{CH}_2\text{Cl}_2$ /n-hexane to give 0.47 g (90% yield) of IIIb. Using the same procedure IIIa was obtained in 80% yield.

*Reaction of II with  $\text{C}_6\text{H}_5\text{NCS}$*

$\text{C}_6\text{H}_5\text{NCS}$  (40 mmol) was added to a solution of 0.45 g (1 mmol) of II in 20 ml of benzene, the mixture was then stirred at room temperature for 24 h. The solvent was removed under vacuum and the residue crystallized from  $\text{CH}_2\text{Cl}_2$ /n-hexane to give 0.49 g (85% yield) of IVb. Using the same procedure IVa was obtained in 80% yield.

*Reaction of  $\eta^5\text{-C}_5\text{H}_5\text{NiPBu}_3\text{Cl}$  with  $\text{NaSC}(\text{NHC}_6\text{H}_5)=\text{C}(\text{CN})_2$*

A mixture of  $\eta^5\text{-C}_5\text{H}_5\text{NiPBu}_3\text{Cl}$  (0.36 g, 1 mmol) and  $\text{NaSC}(\text{NHC}_6\text{H}_5)=\text{C}(\text{CN})_2$  (0.66 g, 3 mmol) in 20 ml benzene was stirred at room temperature for 3 h. The solution was evaporated to dryness under vacuum and the residue crystallized from benzene/n-hexane to give 0.37 g (70% yield) of IIIb. Using the same procedure IVb was obtained in 85% yield.

*Reaction of IIIb with  $\text{PBu}_3$*

When 0.20 g (1 mmol) of  $\text{PBu}_3$  was added to a solution of IIIb (0.53 g, 1 mmol) in 20 ml  $\text{CH}_2\text{Cl}_2$ , the color of the solution immediately changed from brown-red to green. The solution was evaporated to dryness under vacuum and the residue crystallized from  $\text{CH}_2\text{Cl}_2$ /ether to afford Vb (0.65 g, 90% yield). Using the same procedure Va was obtained in 90% yield.

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