

## Preliminary communication

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### $\pi$ -Cyclopentadienyls of nickel(II)

#### X. Phenylisothiocyanate insertion into $\pi$ -C<sub>5</sub>H<sub>5</sub>NiPBu<sub>3</sub>SC<sub>2</sub>H<sub>5</sub>

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(Received October 16th, 1972)

#### SUMMARY

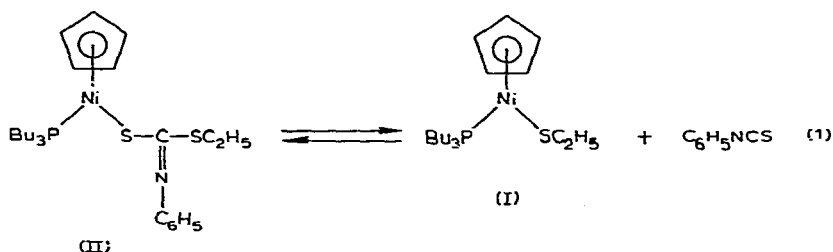
$[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{PBu}_3)(\text{SC}_2\text{H}_5)]$  reacts with PhNCS to give  $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{PBu}_3)\{\text{SC}(=\text{NPh})\text{SC}_2\text{H}_5\}]$ ; the product reversibly dissociates to the reactants in solution.

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It has been shown previously that  $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SR}$  complexes readily undergo carbon disulfide insertion to produce the stable (alkyltrithiocarbonato)nickel complex<sup>1</sup>. We describe below phenylisothiocyanate insertion into the complex  $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SC}_2\text{H}_5$ , and some properties of the product.

After standing a few hours at room temperature, a mixture of  $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SC}_2\text{H}_5$  (I) and an excess of C<sub>6</sub>H<sub>5</sub>NCS in pentane gave reddish brown crystals in quantitative yield; these had the molecular formula  $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SC}_2\text{H}_5 \cdot \text{C}_6\text{H}_5\text{NCS}$  (II), m.p. 70.5–71.5° (Found: C, 59.25; H, 7.98; N, 2.71. C<sub>26</sub>H<sub>42</sub>NNiPS<sub>2</sub> calcd.: C, 59.84; H, 8.05; N, 2.68%). The product (II) appeared to be an *S*- rather than an *N*-dithiocarbamate-nickel complex, since the IR spectrum of the solid showed no band which might be assigned to a C=S stretching mode, but a strong band was observed at 1530 cm<sup>-1</sup>, and is assigned to  $\nu(\text{C}=\text{N})^2$ .

Cryoscopy in benzene, and the IR spectrum and NMR spectrum of (II) showed that the complex (II) dissociated in organic solvents such as benzene, hexane and acetone according to Eq.1. The apparent molecular weight of (II) (291), in benzene is lower than the calculated values (522). The IR spectrum of complex (II) in organic solvents showed a band at near 2100 cm<sup>-1</sup> characteristic of  $-\text{N}=\text{C}=\text{S}$  str. which was not present in solid (II). The proton NMR spectrum of (II) in C<sub>6</sub>D<sub>6</sub> showed, in addition to the peaks which were assigned to the phenyl and PBu<sub>3</sub> protons, a quartet at  $\tau$  6.86 due to the methylene protons of S–C<sub>2</sub>H<sub>5</sub> in (II), a quartet at  $\tau$  7.88 due to the methylene protons of S–C<sub>2</sub>H<sub>5</sub> in (I)<sup>3</sup>,



and a singlet at  $\tau$  4.82 due to the  $\pi$ -cyclopentadienyl protons of (I) and (II) (Table 1). It is interesting that the chemical shifts of the  $\pi$ -cyclopentadienyl protons of (I) and (II) in C<sub>6</sub>D<sub>6</sub> were identical, but in CD<sub>3</sub>COCD<sub>3</sub> they had different shifts, and appeared at  $\tau$  4.80 and 4.72, respectively.

TABLE 1

## THE PROTON NMR SPECTRAL DATA

Solvent	Chemical shift (internal TMS)			
	$\tau$ (C <sub>6</sub> H <sub>5</sub> )	$\tau$ ( $\pi$ -C <sub>5</sub> H <sub>5</sub> )	$\tau$ (S-CH <sub>2</sub> -C $\equiv$ )	$\tau$ (PBu <sub>3</sub> ) + $\tau$ (S-CH <sub>2</sub> )
C <sub>6</sub> D <sub>6</sub>	2.6-3.5	4.82	6.86 <sup>b</sup>	8.2-9.4
	(m, 5H) <sup>a</sup>	(s, 5H)	(q, 0.9H) 7.88 <sup>c</sup>	(30H)
CD <sub>3</sub> COCD <sub>3</sub>	2.4-3.3	4.72 <sup>b</sup>	7.08 <sup>b</sup>	7.8 ~ 9.2 <sup>d</sup>
	(m, 5H)	(s, 3H)	(q, 1.2H)	
		4.80 <sup>c</sup> (s, 2H)	8.14 <sup>c,d</sup>	

<sup>a</sup> m, multiplet; s, singlet; q, quartet. <sup>b</sup> Assigned to complex II. <sup>c</sup> Assigned to complex I. <sup>d</sup> The signals from the methylene protons were overlapped by signals from the solvent and PBu<sub>3</sub> protons.

## REFERENCES

- 1 F. Sato, K. Iida and M. Sato, *J. Organometal. Chem.*, 39 (1972) 197.
- 2 M.F. Lappert and A.R. Sanger, *J. Chem. Soc. A*, (1971) 1314.
- 3 M. Sato and T. Yoshida, *J. Organometal. Chem.*, 39 (1972) 389.

*J. Organometal. Chem.*, 46 (1972)