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# THE SYNTHESIS AND SOME PROPERTIES OF TRI-n-BUTYLPHOSPHINE-$\pi$-CYCLOPENTADIENYLNICKEL MERCAPTIDES

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## SUMMARY

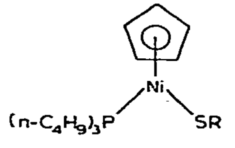
Complexes of the general formula $\pi$-$C_5H_5Ni[P(n\text{-}C_4H_9)_3]SR$ (I) (where R is H, $CH_3$, $C_2H_5$, n-$C_3H_7$, n-$C_4H_9$, $CH_2C_6H_5$, $CH_2COOH$, and $COCH_3$) and $\pi$-$C_5H_5Ni[P(n\text{-}C_4H_9)_3]SC_6H_4X$ (II) (where X is H, *p*-$CH_3$, *p*-Cl, *p*-$COCH_3$, and *p*-$NO_2$) have been prepared. Their IR and NMR spectra have been studied, and the C–H out-of-plane bending vibrations and the $^1H$ chemical shifts of the $\pi$-cyclopentadienyl group found to show a linear correlation with the Taft $\sigma^*$-constants of R in (I) and with the Hammett $\sigma$-constants of X in (II).

## INTRODUCTION

We previously reported the syntheses of the complexes $\pi$-$C_5H_5Ni[P(n\text{-}C_4H_9)_3]X$ (X=anionic ligands)[1] and of some $\pi$-cyclopentadienylnickel derivatives containing sulfur ligands[2], but we did not carry out an analysis of their spectra. Recently spectroscopic studies of $\pi$-cyclopentadienyl groups in $\pi$-cyclopentadienylmetal compounds have been reported by several workers[3-5], but there has been no quantitative investigation of the effect of SR ligands on the spectroscopic properties of the $\pi$-cyclopentadienyl group. We now describe the synthesis of a series of alkyl and *p*-substituted phenyl mercaptide complexes, and discuss the IR and NMR spectroscopic properties of the $\pi$-cyclopentadienyl group in these complexes.

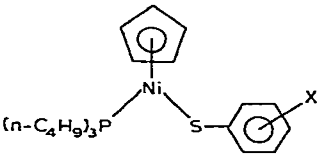
## RESULT AND DISCUSSION

The appropriate sodium mercaptide reacted readily in aqueous solution with $\{\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]_2\}^+Cl^-$ to give complexes of types (I) and (II). In the case



(I)

R=H, $CH_3$, $C_2H_5$, n-$C_3H_7$,
n-$C_4H_9$, $CH_2C_6H_5$,
$CH_2COOH$, $COCH_3$



(II)

X= *p*-$CH_3$, H, *p*-Cl,
*p*-$COCH_3$, *p*-$NO_2$

of thioglycolic acid, the type (I) complex was synthesized by the reaction of thioglycolic acid with $\{\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]_2\}^+Cl^-$ in the presence of triethylamine. The yields were comparatively high in most cases.

These complexes are soluble in benzene, n-hexane and n-pentane, but react slowly at room temperature with methylene chloride and carbon tetrachloride to give the known complex $\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]Cl$. The physical properties of the complexes (I) and (II) are listed in Tables 1 and 2.

The IR spectra of the complexes (I) and (II) resemble that of $\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]Cl$ except for the presence of additional absorptions characteristic of the R and $C_6H_4X$ groups. It is obvious from the data that the C–H out-of-plane bending vibrations of the $\pi\text{-}C_5H_5$ group depend on the nature of the R groups in the complexes (I) or the X groups in the complexes (II), although the variations are small.

TABLE 1

SOME PROPERTIES OF $\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]SR$

| *R* | *M.p. (°C)* | *Color* | *IR (cm$^{-1}$)$^a$ $\gamma(C_5H_5)$* | *$^1H$ NMR ($\tau$)$^b$* | |
|---|---|---|---|---|---|
| | | | | *$C_5H_5$* | *R* |
| n-$C_4H_9$ | Oil | Green-brown | 776 | 4.82 (s, 5H) | 7.85 (t, $J_{\alpha,\beta}$ 5.5 Hz, 2H)$^e$ |
| n-$C_3H_7$ | 41–41 | Green | 776 | 4.82 (s, 5H) | 7.85 (t, $J_{\alpha,\beta}$ 5.5 Hz, 2H)$^e$ |
| $C_2H_5$ | 53–54 | Green | 776 | 4.82 (s, 5H) | 7.85 (q, $J_{\alpha,\beta}$ 6.0 Hz, 2H)$^e$ |
| $CH_3$ | Oil | Green-brown | 777 | 4.85 (s, 5H) | 8.20 (s, 3H) |
| $CH_2C_6H_5$ | 38–39$^c$ | Brown | 778 | 4.84 (s, 5H) | 2.35–3.10 (m)$^f$, 6.70 (s, 2H) |
| H | 51–52 | Brown | 779 | 4.86 (s, 5H) | 4.71 (s, 1H) |
| $C_6H_5$ | 51–52$^d$ | Green | 779 | 4.80 (s, 5H) | 1.90–2.13 and 2.70–3.15 (m)$^f$ |
| $CH_2COOH$ | 77–79 | Brown | 780 | 4.74 (s, 5H) | 7.97 (s, 2H) |
| $COCH_3$ | 67–68 | Brown | 782 | 4.68 (s, 5H) | 7.55 (s, 3H) |

[a] Measured in Nujol mull. [b] Measured in $C_6D_6$ with TMS as internal reference, multiplicity of peaks: s, singlet; t, triplet; q, quartet; m, multiplet. [c] Ref. 2 gives 31.5–32.0°. [d] Ref. 2 gives 45–46°. [e] Signals of $\beta$, $\gamma$ and $\delta$ hydrogens were overlapped by signals of $P(n\text{-}C_4H_9)_3$ protons. [f] Overlapped by signals of $C_6D_6$ protons.

ABLE 2

OME PROPERTIES OF $\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]SC_6H_4X$

| | *M.p. (°C)* | *Color* | *IR (cm$^{-1}$)$^a$ $\gamma(C_5H_5)$* | *$^1H$ NMR ($\tau$)$^b$* | | |
|---|---|---|---|---|---|---|
| | | | | *$C_5H_5$* | *$SC_6H_4$* | *X* |
| $CH_3$ | 49–50 | Green | 778 | 4.98 (s, 5H) | 2.84 (d, $J_{o,m}$ 7.5 Hz, 2H), 3.44 (d, 2H) | 7.90 (s, 3H |
| | 51–52 | Green | 779 | 4.95 (s, 5H) | 2.62–2.83 and 3.13–3.42 (m, 5H) | |
| Cl | 63–64 | Green | 782 | 4.91 (s, 5H) | 2.61 (d, $J_{o,m}$ 8.0 Hz, 2H), 3.29 (d, 2H) | |
| $COCH_3$ | 79–80 | Brown | 784 | 4.85 (s, 5H) | 2.57 (d, $J_{o,m}$ 9.5 Hz, 2H), 2.65 (d, 2H) | 7.69 (s, 3H |
| $NO_2$ | 113–114 | Brown | 792 | 4.81 (s, 5H) | 2.38 (d, $J_{o,m}$ 10 Hz, 2H), 2.52 (d, 2H) | |

Measured in Nujol mull. [b] Measured in $CS_2$ using TMS as internal reference: multiplicity of peaks: s, single doublet; m, multiplet.

It has been claimed that the C–H out-of-plane bending vibration of the aromatic system is related to the π-electron density of the aromatic rings, a high value being indicative of a relatively low π-electron density[6]. This suggestion can be applied to the π-$C_5H_5$ ring, and it is known that the π-electron density of the π-$C_5H_5$ group in π-cyclopentadienylmetal compounds is closely related to the charge density on the transition metal[3]. On the other hand, Kreevoy and his co-workers[7] have concluded that a linear relationship between the acid dissociation constants of mercaptans and the Taft $\sigma^*$-constants of the substituents depends on the inductive effects of the substituents. Thus we examined the relationship between the C–H out-of-plane bending vibrations of the π-$C_5H_5$ group and Taft $\sigma^*$-constants. As can be seen in Fig. 1, there is a good linear relationship, which indicates that the inductive effects of the R groups in the type (I) complexes affect the π-electron density in the π-$C_5H_5$ group by transmission through the sulfur-nickel bond. In Fig. 2, the wave numbers of the C–H out-of-plane bending vibrations are plotted against the Hammett σ-constants of the substituents of X in the type (II) complexes, and again there is a linear correlation. The C–H out-of-plane bending vibrations of the π-$C_5H_5$ group would be affected by transmission of the overall polar effect of the X group to the benzene ring via the sulfur–nickel bond.

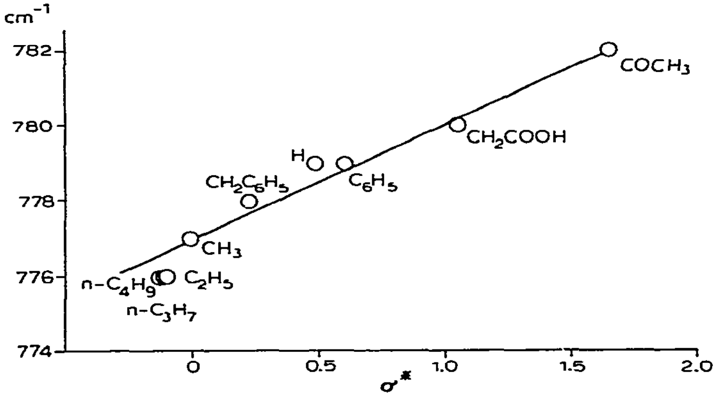


Fig. 1. Plot of $\gamma(C_5H_5)$ against $\sigma^*$ for π-$C_5H_5Ni[P(n\text{-}C_4H_9)_3]SR$.

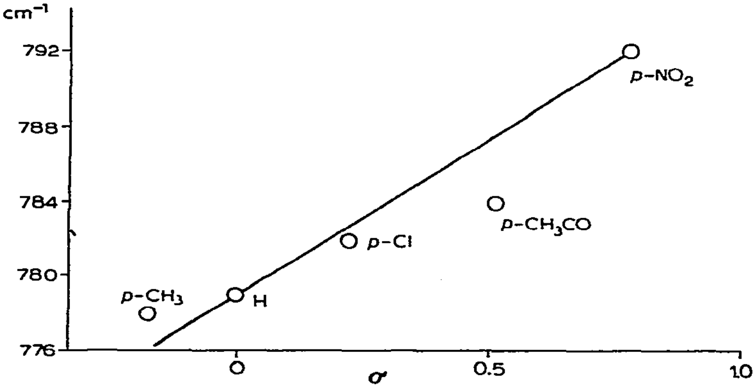


Fig. 2. Plot of $\gamma(C_5H_5)$ against σ for π-$C_5H_5Ni[P(n\text{-}C_4H_9)_3]SC_6H_4X$.

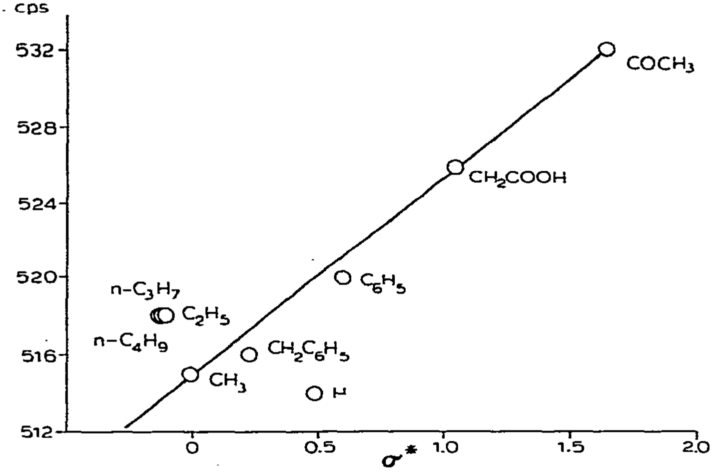


Fig. 3. Plot of chemical shift of $\pi$-$C_5H_5$ against $\sigma^*$ for $\pi$-$C_5H_5Ni[P(n\text{-}C_4H_9)_3]SR$.

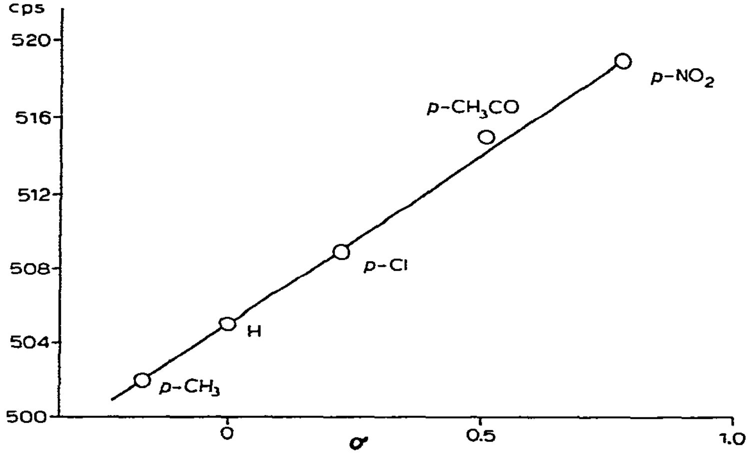


Fig. 4. Plot of chemical shift of $\pi$-$C_5H_5$ against $\sigma$ for $\pi$-$C_5H_5Ni[P(n\text{-}C_4H_9)_3]SC_6H_4X$.

The NMR spectra of the complexes (I) and (II) show a signal at $\tau$ 8.30–9.25 due to the $P(n\text{-}C_4H_9)_3$ protons and a sharp singlet at around $\tau$ 4.90 due to the $\pi$-$C_5H_5$ protons. While in the type (I) complexes the signals of the R groups appear at the expected positions, in type (II) complexes the resonances of the phenyl protons appear as an AB doublet when X is $p$-$COCH_3$ or $p$-$NO_2$ and as an AX doublet when X is $p$-$CH_3$ or $p$-Cl (Tables 1 and 2). The $^1H$ chemical shifts of the $\pi$-$C_5H_5$ group are linearly related to the Taft $\sigma^*$-constants of R in the type (I) complexes and to the Hammett $\sigma$-constants of X in the type (II) complexes, as shown in Figs. 3 and 4, respectively.

We conclude that the inductive effect of the R groups and the overall polar effect of the X groups are transmitted through the sulfur–nickel bond to influence the $\pi$-electron density in the $\pi$-$C_5H_5$ ring.

## EXPERIMENTAL

Complex $\{\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]_2\}^+Cl^-$ was prepared as previously described[8]. All the mercaptans except 4-acetylphenyl mercaptan were commercial samples, and were used without further purification. 4-Acetylphenyl mercaptan was obtained by Overberger's method[9]. All the solvents were purified and degassed before use, and all experiments were conducted under dry nitrogen.

The Taft $\sigma^*$-constants of the R groups and the Hammett $\sigma$-constants of the X groups were taken from ref. 10.

IR spectra were recorded with Nujol mulls on a Perkin-Elmer model 125 spectrometer. NMR spectra were recorded on a JEOL-JNM-4H100 NMR spectrometer with tetramethylsilane as internal standard. Solvent effects were minimized by taking all measurements at approximately the same concentration (ca. 8% w/v).

*Reaction of* $\{\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]_2\}^+Cl^-$ *with sodium methyl mercaptide*

An aqueous solution of $\{\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P(n-C}_4\text{H}_9)_3]_2\}^+\text{Cl}^-$ (3 mmoles) was added to an aqueous solution of sodium methyl mercaptide (3 mmoles) at room temperature under dry nitrogen. Reaction occurred immediately and a brown oil was formed. This was extracted with benzene, and the benzene solution was dried over anhydrous calcium chloride. The benzene was removed under vacuum to leave a brown residue. Recrystallization from n-pentane gave 0.63 g (56% yield) of green-brown oily product. (Found: C, 57.76; H, 9.50; S, 8.93. $C_{18}H_{35}NiPS$ calcd.: C, 57.95; H, 9.39; S, 8.59%.)

*Reaction of* $\{\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]_2\}^+Cl^-$ *with sodium ethyl mercaptide*

Similarly, $\{\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P(n-C}_4\text{H}_9)_3]_2\}^+\text{Cl}^-$ (3 mmoles) and sodium ethyl mercaptide (3 mmoles) gave 0.83 g (74% yield) of green crystals, m.p. 53–54°. (Found: C, 58.34; H, 9.09; S, 7.90. $C_{19}H_{37}NiPS$ calcd.: C, 58.96; H, 9.56; S, 8.27%.)

*Reaction of* $\{\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]_2\}^+Cl^-$ *with sodium n-propyl mercaptide*

$\{\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P(n-C}_4\text{H}_9)_3]_2\}^+\text{Cl}^-$ (3 mmoles) and sodium n-propyl mercaptide (3 mmoles) gave 0.85 g (72% yield) of green crystals, m.p. 41–42°. (Found: C, 59.89; H, 9.70; S, 8.59. $C_{20}H_{39}NiPS$ calcd.: C, 59.89; H, 9.73; S, 7.98%.)

*Reaction of* $\{\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]_2\}^+Cl^-$ *with sodium n-butyl mercaptide*

$\{\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P(n-C}_4\text{H}_9)_3]_2\}^+\text{Cl}^-$ (3 mmoles) and sodium n-butyl mercaptide (3 mmoles) gave 0.55 g (41% yield) of a green-brown oil. (Found: C, 59.96; H, 10.67. $C_{21}H_{41}NiPS$ calcd.: C, 60.79; H, 9.90%.)

*Reaction of* $\{\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]_2\}^+Cl^-$ *with sodium thioacetic acid*

$\{\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P(n-C}_4\text{H}_9)_3]_2\}^+\text{Cl}^-$ (3 mmoles) and sodium thioacetic acid (3 mmoles) gave 1.13 g (86% yield) of brown crystals, m.p. 67–68°. (Found: C, 56.60; H, 9.37; S, 7.91. $C_{19}H_{35}NiOPS$ calcd.: C, 56.90; H, 8.75; S, 8.00%.)

*Reaction of* $\{\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]_2\}^+Cl^-$ *with sodium 4-methylphenyl mercaptide*

$\{\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P(n-C}_4\text{H}_9)_3]_2\}^+\text{Cl}^-$ (3 mmoles) and sodium 4-methylphenyl mercaptide (3 mmoles) gave 1.12 g (83% yield) of green crystals, m.p. 49–50°. (Found: C, 63.92; H, 8.59; S, 6.88. $C_{24}H_{39}NiPS$ calcd.: C, 64.19; H, 8.69; S, 7.13%.)

*Reaction of* $\{\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]_2\}^+Cl^-$ *with sodium 4-chlorophenyl mercaptide*

$\{\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P(n-C}_4\text{H}_9)_3]_2\}^+\text{Cl}^-$ (3 mmoles) and sodium 4-chlorophenyl mercaptide (3 mmoles), gave 1.25 g (89% yield) of green crystals, m.p. 63–64°. (Found: C, 58.57; H, 7.85. $C_{23}H_{36}ClNiPS$ calcd.: C, 58.82; H, 7.69%.)

*Reaction of* $\{\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]_2\}^+Cl^-$ *with sodium 4-acetylphenyl mercaptide*

Similarly, but with recrystallization from n-hexane, $\{\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]_2\}^+Cl^-$ (3 mmoles) with sodium 4-acetylphenyl mercaptide (3 mmoles) gave 1.11 g (77% yield) of brown crystals, m.p. 79–80°. (Found: C, 62.86; H, 8.23; S, 6.91. $C_{25}H_{39}NiOPS$ calcd.: C, 62.93; H, 8.18; S, 6.71%.)

*Reaction of* $\{\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]_2\}^+Cl^-$ *with sodium 4-nitrophenyl mercaptide*

Similarly, but with recrystallization from benzene/n-hexane, $\{\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]_2\}^+Cl^-$ (3 mmoles) and sodium 4-nitrophenyl mercaptide (3 mmoles) gave 1.30 g (87% yield) of brown crystals, m.p. 113–114°. (Found: C, 57.48; H, 8.26; S, 6.49. $C_{23}H_{36}NNiOPS$ calcd.: C, 57.54; H, 7.52; S, 6.67%.)

*Reaction of* $\{\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]_2\}^+Cl^-$ *with thioglycolic acid in the presence of triethylamine*

An aqueous solution of $\{\pi\text{-}C_5H_5Ni[P(n\text{-}C_4H_9)_3]_2\}^+Cl^-$ (3 mmoles) was added to an aqueous solution of thioglycolic acid (3 mmoles) in the presence of triethylamine (3 mmoles) at room temperature. A brown precipitate immediately formed. The mixture was extracted with benzene, and the benzene solution was dried over anhydrous calcium chloride. The benzene was removed under vacuum, and recrystallization from benzene/n-hexane gave 0.79 g (62% yield) of brown solid, m.p. 77–79°. (Found: C, 54.22; H, 8.56. $C_{19}H_{35}NiO_2PS$ calcd.: C, 54.67; H, 8.39%.)

## REFERENCES

1 M. Sato, F. Sato and T. Yoshida, *J. Organometal. Chem.*, 31 (1971) 415.
2 M. Sato, F. Sato, N. Takemoto and K. Iida, *J. Organometal. Chem.*, 34 (1972) 205.
3 R. B. King, *Inorg. Chim. Acta*, 2 (1968) 454.
4 A. N. Nesmeyanov, K. N. Anisimov, B. V. Loksin, N. E. Kolobova and Y. K. Makarov, *Dokl. Akad. Nauk SSSR*, 176 (1967) 182.
5 D. S. Field and M. J. Newlands, *J. Organometal. Chem.*, 27 (1971) 213.
6 R. D. Kross, V. A. Fassel and M. Margoshes, *J. Amer. Chem. Soc.*, 78 (1956) 1332.
7 M. K. Kreevoy, E. T. Happer, R. E. Duval, H. S. Wilgus, III, and L. T. Ditsh, *J. Amer. Chem. Soc.*, 82 (1960) 4899.
8 M. Sato, F. Sato and T. Yoshida, *J. Organometal. Chem.*, 27 (1971) 273.
9 C. G. Overberger and A. Lebovits, *J. Amer. Chem. Soc.*, 78 (1956) 4792.
10 R. W. Taft in M. S. Newman, *Steric Effects in Organic Chemistry*, Wiley, New York, N.Y., Chap. 13.