

SELENIUM AND TELLURIUM DERIVATIVES OF π -CYCLOPENTADIENYLNICKEL TRI-*n*-BUTYLPHOSPHINE

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SUMMARY

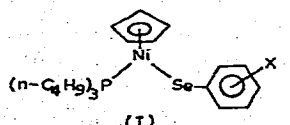
Complexes of the general formula π -C₅H₅Ni[P(*n*-C₄H₉)₃]SeC₆H₄X (I) (where X is H, *p*-CH₃O, *p*-CH₃, *p*-Cl, *m*-Cl, *m*-CF₃, and *p*-CH₃CO) and π -C₅H₅Ni[P(*n*-C₄H₉)₃]TeC₆H₄X (II) (where X is H, *p*-CH₃O, *p*-CH₃, *p*-Cl, and *m*-CF₃) have been prepared and their NMR spectra recorded. Good correlations exist between the ¹H chemical shifts of the π -C₅H₅ group and the Hammett σ -constants of X for both (I) and (II). The Hammett ρ values were found to be -18.7 and -19.3 (in Hz/ σ) for (I) and (II). These values are compared with those obtained for the analogous sulfur complexes.

INTRODUCTION

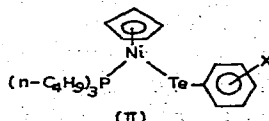
Transition metal complexes containing selenium and tellurium as donor atoms have recently been prepared and characterized¹⁻³, but the π -cyclopentadienylnickel compound with selenium and tellurium ligands has not been prepared. In the present work, we wish to report the synthesis of the complexes of π -cyclopentadienylnickel with *m*- and *p*-substituted phenyl selenides and tellurides, and discuss the nature of nickel-sulfur, -selenium, and -tellurium bonds in these complexes.

RESULTS AND DISCUSSION

The NaEC₆H₄X compounds (E=Se, Te) reacted readily in aqueous or ethanolic solutions with $\{\pi$ -C₅H₅Ni[P(*n*-C₄H₉)₃]₂}⁺Cl⁻ to give the complexes (I) and (II). The yields were fairly high in most cases.



X = *p*-CH₃O, *p*-CH₃, H, *p*-Cl,
m-Cl, *m*-CF₃, *p*-CH₃CO



X = *p*-CH₃O, *p*-CH₃, H,
p-Cl, *m*-CF₃

These complexes (I) and (II) are stable under dry nitrogen, and fairly stable even under air at room temperature. The complexes (I) and (II) are soluble in benzene, n-hexane and n-pentane, but react slowly at room temperature with methylene chloride and carbon tetrachloride to give the complex $\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]\text{Cl}$.

The complexes $\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]\text{EC}_6\text{H}_4\text{X}$ reacted with methyl iodide in benzene solution to give $\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]\text{I}$ and $\text{CH}_3\text{EC}_6\text{H}_4\text{X}$. The physical properties of the complexes (I) and (II) are shown in Table 1 and 2.

TABLE 1

SOME PROPERTIES OF $\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]\text{SeC}_6\text{H}_4\text{X}^a$

X	M.p. (°C)	$^1\text{H NMR}(\tau)^b$		
		C_5H_5	SeC_6H_4	X
p-CH ₃ O	42-43	4.98(s,1H)	2.68(d, J_{om} 9.0 Hz, 2H), 3.60(d, 2H)	6.36(s,3H)
p-CH ₃	53-54	4.96(s,1H)	2.68(d, J_{om} 7.5 Hz, 2H), 3.38(d, 2H)	7.87(s,3H)
H	51-52	4.94(s,1H)	2.50-2.59 and 3.02-3.29(m, 5H)	
p-Cl	63-64	4.90(s,1H)	2.46(d, J_{om} 8.0 Hz, 2H) 3.26(d, 2H)	
m-Cl	36-37	4.87(s,1H)	2.38(s, 1H) 2.63(d, J 6.0 Hz, 1H) 3.10-3.32(m, 2H)	
m-CF ₃	62-63	4.85(s,1H)	2.03(s, 1H) 2.32(d, J 7.5 Hz, 1H) 2.90-3.03(m, 2H)	
p-CH ₃ CO	65-66	4.83(s,1H)	2.35(d, J_{om} 8.5 Hz, 2H) 2.65(d, 2H)	7.66(s, 3H)

^a All compounds are green. ^b Measured in CS₂ using TMS as internal standard: multiplicity of peaks: s, singlet; d, doublet; m, multiplet.

TABLE 2

SOME PROPERTIES OF $\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]\text{TeC}_6\text{H}_4\text{X}^a$

X	M.p. (°C)	$^1\text{H NMR}(\tau)^b$		
		C_5H_5	TeC_6H_4	X
p-CH ₃ O	53-54	4.98(s,1H)	2.54(d, J_{om} 8.0 Hz, 2H) 3.62(d, 2H)	6.22(s, 3H)
p-CH ₃	38-39	4.95(s,1H)	2.54(d, J_{om} 7.5 Hz, 2H) 3.37(d, 2H)	7.79(s, 3H)
H	49-50 ^c	4.93(s,1H)	2.40-2.47 and 3.00-3.32(m, 5H)	
p-Cl	47-48	4.89(s,1H)	2.44(d, J_{om} 9.0 Hz, 2H) 3.25(d, 2H)	
m-CF ₃	43-44	4.84(s,1H)	2.01(s, 1H) 2.18(d, J 7.5 Hz, 1H) 2.79-3.11(m, 2H)	

^{a,b} See Table 1. ^c Brown.

The NMR spectra of the complexes (I) and (II) show a signal at τ 8.30-9.25 ppm due to the P(n-C₄H₉)₃ protons, and a sharp singlet at around τ 4.90 ppm due to the $\pi\text{-C}_5\text{H}_5$ protons. The resonance of the phenyl protons and of the substituents X appear at the expected positions. It is obvious from Tables 1 and 2 that the ^1H chemical shifts of the $\pi\text{-C}_5\text{H}_5$ group depend on the nature of the X groups in the complexes (I) and (II), electron-releasing groups increasing the ^1H chemical shifts of the $\pi\text{-C}_5\text{H}_5$ group and electron-attracting groups decreasing them. Thus as in the case of the complex $\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]\text{SC}_6\text{H}_4\text{X}^4$, we determined to plot the ^1H chemical shifts of the $\pi\text{-C}_5\text{H}_5$ group against the Hammett σ -constants of X in the complexes (I)

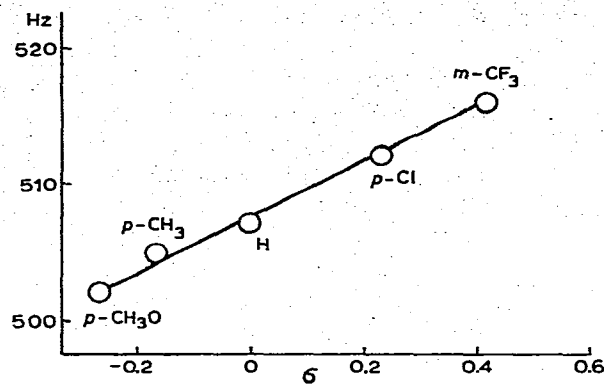
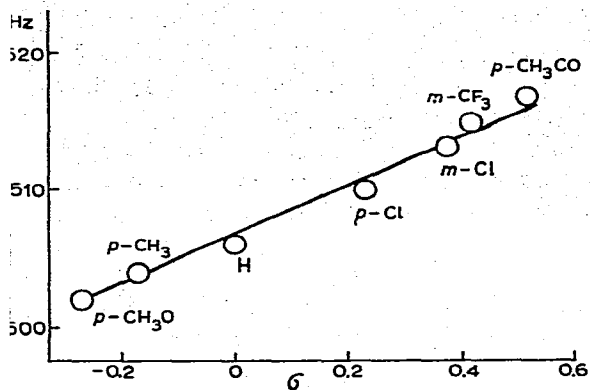


Fig. 1. Plot of chemical shift of $\pi\text{-C}_5\text{H}_5$ against σ for $\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]\text{SeC}_6\text{H}_4\text{X}$.

Fig. 2. Plot of chemical shift of $\pi\text{-C}_5\text{H}_5$ against σ for $\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]\text{TeC}_6\text{H}_4\text{X}$.

and (II). As can be seen from Figs. 1 and 2, there are good linear relationships for both sets of complexes. The results indicate that the overall polar effects of the X groups to phenyl ring affect the ^1H chemical shifts of the $\pi\text{-C}_5\text{H}_5$ group (that is, the π -electron density of the $\pi\text{-C}_5\text{H}_5$ group) by transmission through the Se-Ni and Te-Ni bonds, as they do through the S-Ni bond in $\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]\text{SC}_6\text{H}_4\text{X}^4$.

From Table 1 and 2, slopes (ρ values) are calculated against σ values by the method of least squares to be $-18.7 \text{ Hz}/\sigma$ for (I) and $-19.3 \text{ Hz}/\sigma$ for (II). The ρ values, together with that for the analogous sulfur complex $\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]\text{SC}_6\text{H}_4\text{X}$ (calculated from ref. 4) are in Table 3. The values imply that the increasing

TABLE 3

$\rho(\text{Hz}/\sigma)$	
Sulfur ligand	-17.9
Selenium ligand	-18.7
Tellurium ligand	-19.3

order of transmission of the polar effects of the X groups through the Ni-E bonds, to influence the π -electron density in the $\pi\text{-C}_5\text{H}_5$ ring, is $\text{S} < \text{Se} < \text{Te}$. The ρ values would largely be determined by the extent of the donor properties of E and the back-coordination, if d_π back-bonding between the filled metallic nickel orbitals and the empty Group VI donor atom (E) orbitals of suitable energy is possible. The larger the donor ability of E, the larger the ρ values⁵. On the other hand, assuming that conjugation between the phenyl ring and E is possible, the extent of the d_π back-bonding will be increased by electron-attracting substituents, since these would tend to attract electrons from E⁶. The back-bonding should therefore cause a downfield shift in the ^1H chemical shifts of the $\pi\text{-C}_5\text{H}_5$ group in proportion to the Hammett σ -constants and consequently give the larger slope (ρ). Unfortunately, the data do not permit unambiguous conclusions about the Ni-E bond character in the complexes.

EXPERIMENTAL

Complex $\{\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]_2\}^+\text{Cl}^-$ was prepared as previously described⁷. All the selenophenols except 4-acetylselenophenol were obtained by Foster's method⁸. 4-Acetylselenophenol was obtained from the reaction of 4-acetylphenyl selenocyanate with sodium⁹. All the tellurophenols were prepared by Giv'a's method¹⁰. All the solvents were purified and degassed before use, and all experiments were conducted under dry nitrogen.

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).

Reactions of $\{\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]_2\}^+\text{Cl}^-$

With NaSeC₆H₅. An aqueous solution of $\{\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]_2\}^+\text{Cl}^-$ (3 mmoles) was added to an aqueous solution of sodium selenophenolate (3 mmoles) at room temperature under dry nitrogen. Reaction occurred immediately, and a green 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 green residue. Recrystallization from n-pentane gave 1.16 g (85% yield) of green crystals, m.p. 51–52°. (Found: C, 57.40; H, 8.15. C₂₃H₃₇NiPSe calcd.: C, 57.30; H, 7.68%.)

With NaSeC₆H₄(4-CH₃O). Similarly, $\{\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]_2\}^+\text{Cl}^-$ (3 mmoles) and sodium 4-methoxyselenophenolate (3 mmoles) gave 1.37 g (89% yield) of green crystals, m.p. 42–43°. (Found: C, 55.73; H, 7.61. C₂₄H₃₉NiOPSe calcd.: C, 56.25; H, 7.62%.)

With NaSeC₆H₄(4-CH₃). $\{\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]_2\}^+\text{Cl}^-$ (3 mmoles) and sodium 4-methylselenophenolate (3 mmoles) gave 1.10 g (74% yield) of green crystals, m.p. 53–54°. (Found: C, 58.46; H, 8.10. C₂₄H₃₉NiPSe calcd.: C, 58.10; H, 7.89%.)

With NaSeC₆H₄(4-Cl). $\{\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]_2\}^+\text{Cl}^-$ (3 mmoles) and sodium 4-chloroselenophenolate (3 mmoles) gave 1.34 g (87% yield) of green crystals, m.p. 63–64°. (Found: C, 53.22; H, 7.29. C₂₃H₃₆ClNiPSe calcd.: C, 53.46; H, 6.99%.)

With NaSeC₆H₄(3-Cl). $\{\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]_2\}^+\text{Cl}^-$ (3 mmoles) and sodium 3-chloroselenophenolate (3 mmoles) gave 1.03 g (67% yield) of green crystals, m.p. 36–37°. (Found: C, 52.83; H, 7.00. C₂₃H₃₆ClNiPSe calcd.: C, 53.46; H, 6.99%.)

With NaSeC₆H₄(3-CF₃). $\{\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]_2\}^+\text{Cl}^-$ (3 mmoles) and sodium 3-(trifluoromethyl)selenophenolate (3 mmoles) gave 1.18 g (72% yield) of green crystals, m.p. 62–63°. (Found: C, 53.28; H, 6.73. C₂₄H₃₆F₃NiPSe calcd.: C, 52.40; H, 6.55%.)

With NaSeC₆H₄(4-CH₃CO). Similarly, but with reaction in ethanol solution, $\{\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]_2\}^+\text{Cl}^-$ (3 mmoles) and sodium 4-acetylselenophenolate (3 mmoles) gave 1.21 g (77% yield) of green crystals, m.p. 65–66°. (Found: C, 56.88; H, 7.54. C₂₅H₃₉NiOPSe calcd.: C, 57.28; H, 7.45%.)

With NaTeC₆H₅. $\{\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]_2\}^+\text{Cl}^-$ (3 mmoles) and sodium tellurophenolate (3 mmoles) gave 1.29 g (81% yield) of brown crystals, m.p. 49–50°. (Found: C, 50.70; H, 6.89. C₂₃H₃₇NiPTe calcd.: C, 52.05; H, 6.98%.)

With NaTeC₆H₄(4-CH₃O). $\{\pi\text{-C}_5\text{H}_5\text{Ni}[\text{P}(\text{n-C}_4\text{H}_9)_3]_2\}^+\text{Cl}^-$ (3 mmoles) and sodium 4-methoxytellurophenolate (3 mmoles) gave 1.39 g (83% yield) of green

crystals, m.p. 53–54°. (Found: C, 51.05; H, 7.03. C₂₄H₃₉NiOPTe calcd.: C, 51.40; H, 6.98%)

With NaTeC₆H₄(4-CH₃). { π -C₅H₅Ni[P(n-C₄H₉)₃]₂}⁺Cl⁻ (3 mmoles) and sodium 4-methyltellurophenolate (3 mmoles) gave 1.31 g (80% yield) of green crystals, m.p. 38–39°. (Found: C, 53.46; H, 7.18. C₂₄H₃₉NiPTE calcd.: C, 52.96; H, 7.17%.)

With NaTeC₆H₄(4-Cl). { π -C₅H₅Ni[P(n-C₄H₉)₃]₂}⁺Cl⁻ (3 mmoles) and sodium 4-chlorotellurophenolate (3 mmoles) gave 1.29 g (76% yield) of green crystals, m.p. 47–48°. (Found: C, 48.73; H, 6.23. C₂₃H₃₆ClNiPTE calcd.: C, 48.85; H, 6.23%.)

With NaTeC₆H₄(3-CF₃). { π -C₅H₅Ni[P(n-C₄H₉)₃]₂}⁺Cl⁻ (3 mmoles) and sodium 3-(trifluoromethyl)tellurophenolate (3 mmoles) gave 1.58 g (88% yield) of green crystals, m.p. 43–44°. (Found: C, 47.46; H, 6.16. C₂₄H₃₆F₃NiPTE calcd.: C, 48.13; H, 6.02%.)

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