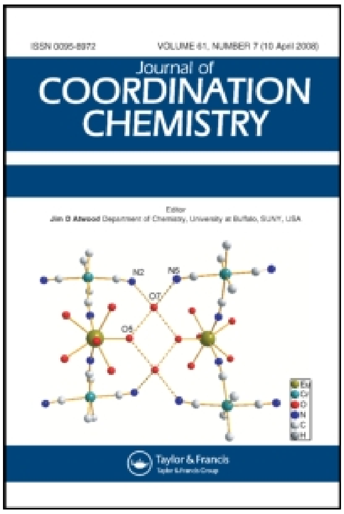

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COMMUNICATION

[2-{DI(p-TOLYL)PHOSPHINO}ETHYL]DIPHENYLPHOSPHINE AND [2-DI(m-TOLYL)PHOSPHINO} ETHYL]DIPHENYLPHOSPHINE COMPLEXES OF NICKEL, PALLADIUM AND PLATINUM(II) CONTAINING M-SH BONDS

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INTRODUCTION

In earlier publications[1,2] we have reported the syntheses of halide and pseudohalide complexes of Ni(II), Pd(II) and Pt(II) containing the novel ditertiary phosphines (m- or p-$CH_3C_6H_4)_2P$-CH_2-CH_2-PPh_2. The complexes have shown to have greater solubilities in organic solvents compared with the well known ditertiary phosphine Ph_2PdlCH_2-CH_2PPh_2. In this paper we wish to report the syntheses of analogous complexes of the two ditertiary phophines with Ni(II), Pd(II) and Pt(II) and which contain vicinal M-SH bonds. Recently monotertiary and ditertiary phosphine complexes of Ni(II), Pd(II) and Pt(II) containing vicinal M-SH and M-SeH groups have been reported.[3-6] In spite of the vicinal groups, the complexes have been shown to exhibit remarkable stability towards air and moisture.

EXPERIMENTAL

Materials and methods

All the chemicals used were of analytical grade. All the solvents were dried and purified by standard methods.[7] The complexes of pptpf and pmtpf, Table I, [M(pptpf)dl)Cl_2] and [M(pmtpf)Cl_2] (M = Ni(II), Pd(II) and Pt(II)) were prepared by the method described earlier.[1,2] All operations were carried out under strictly anhydrous conditions. The solvents were degassed before use and a nitrogen atmosphere was routinely used for carrying out the reactions.

Carbon and hydrogen were estimated by the combustion method, phosphorus was determined as ammonium phosphomolybdate and sulphur as barium sulphate. Infrared spectra were recorded on a Perkin Elmer 621 spectrophotometer. The 90 MHz ^1H n.m.r. spectra were recorded in freshly prepared $CDCl_3$ solutions on a Perkin Elmer R-32 instrument. Tetramethylsilane was used as an internal standard in all cases. Electrical conductance measurements were performed in freshly prepared nitrobenzene solutions on an Elico CM 82T conductivity bridge. Magnetic susceptibilities were measured by the Gouy method.

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TABLE I
Analytical and other data for the complexes.

Compound*	Colour	Dec. Temp. (°)	Analysis % Found (Calcd.) C	H	P	S
[Ni(pptpf)(SH)$_2$]	brown	127	59.8	5.2	10.9	11.4
			(60.0)	(5.5)	(10.25)	(11.6)
[Pd(pptpf)(SH)$_2$]	orange-red	145	56.0	4.9	10.15	10.55
			(56.15)	(5.05)	(10.35)	(10.7)
[Pt(pptpf)(SH)$_2$]	yellow	187	48.75	4.3	8.9	9.15
			(48.9)	(4.4)	(9.0)	(9.3)
[Ni(pmtpf)(SH)$_2$]	brown	123	59.85	5.6	11.0	11.3
			(60.0)	(5.5)	(11.25)	(11.6)
[Pd(pmtpf)(SH)$_2$]	orange-red	134	56.1	4.95	10.2	10.45
			(56.15)	(5.05)	(10.35)	(10.7)
[Pt(pmtpf)(SH)$_2$]	yellow	193	48.8	4.2	8.85	9.2
			(48.9)	(4.4)	(9.0)	(9.3)

*pptpf = [2-{di(p-tolyl)phosphino}ethyl]diphenylphosphine, pmtpf = [2-{di(m-tolyl)phosphino}ethyl] diphenylphosphine.

[Ni(pptpf) (SH)$_2$]

To a solution of sodium hydrogen sulphide (0.28 g, 5.0 mmol) in 25 cm^3 of ethanol and 10 cm^3 of benzene was added [Ni(pptpf)Cl$_2$] (1.39 g, 2.5 mmol). The suspension slowly turned brown and the mixture was stirred for 35–40 hours. The solvent was removed from the reaction mixture, and the residue was washed with water and *n*-hexane, and dried under vacuum to give a brown complex. All other complexes were prepared in an analogous fashion to the above.

The analytical data and colours of all the complexes are given in Table I.

RESULTS AND DISCUSSION

Stable complexes of nickel(II), palladium(II) and platinum(II) containing vicinal M–SH groups were easily prepared by the reaction of the corresponding dichloro complexes of pptpf and pmtpf with sodium hydrogen sulphide in a 1:2 mol ratio. All the Ni(II), Pd(II) and Pt(II) complexes are coloured solids. The complexes are stable towards air and moisture, but decompose on heating. Solutions in chloroform or dichloromethane decompose on standing for some time at room temperature and turn black. The complexes are insoluble in *n*-hexane and petrol.

In the infrared spectra of the complexes a sharp band in the 2400–2600 cm^{-1} region was observed and this was assigned to the ν(SH) vibrations. In addition, two additional vibrations found at 435–450 cm^{-1} and 335–350 cm^{-1} have also been observed (Table II) and were assigned to ν(M--S) vibrations. When the infrared spectra are compared to

TABLE II
Selected infrared data for the complexes (cm^{-1}).

Complex	ν(SH)	ν(M-S)	
[Ni(pptpf)(SH)$_2$]	2540	440	345
[Pd(pptpf)(SH)$_2$]	2470	435	335
[Pt(pptpf)(SH)$_2$]	2460	440	340
[Ni(pmtpf)(SH)$_2$]	2580	438	337
[Pd(pmtpf)(SH)$_2$]	2490	440	340
[Pt(pmtpf)(SH)$_2$]	2470	435	335

those of the corresponding parent compounds $[M(P-P)Cl_2]$[1,2] (where M = Ni(II), Pd(II) or Pt(II); P-P = pptpf or pmtpf, it was observed that the assigned ν(M-Cl) bands are absent. Otherwise the infrared spectra of the $[M(P-P)(SH)_2]$ complexes are similar to the corresponding dichloro complexes.

All the complexes are diamagnetic and non-conducting in nitrobenzene solution. In the proton n.m.r. spectra of the complexes in $CDCl_3$, aromatic protons give a multiplet at δ7.6–7.3, and methyl protons give a singlet at δ2.5–2.3 ppm. In addition to these signals, a singlet at δ1.65–1.5 ppm has also been observed and is assigned to the protons of the -SH groups.

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