

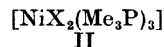
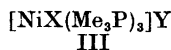
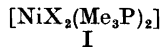
Ni(II) Complexes of Trimethylphosphine

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Tertiary aliphatic phosphines ordinarily form square planar complexes $[\text{NiX}_2(\text{R}_3\text{P})_2]$ with nickel salts. With trimethylphosphine, however, more than two moles of the phosphine can be coordinated to the nickel atom as observed in previous work in this laboratory.¹ Apart from this paper, only Beg and Clark² have published on Ni(II) complexes with trimethylphosphine, namely $[\text{NiX}_2(\text{Me}_3\text{P})_2]$, X = Cl, Br, I, NCS, and NO₂. These compounds were prepared by heating trimethylphosphine and the nickel salts in a 2:1 ratio in sealed tubes, and therefore the ability of trimethylphosphine to form complexes with a higher phosphine to nickel ratio was not observed.

Complexes of types I–IV have now been prepared with a variety of anions. The analyses and some physical properties of



the compounds prepared are listed in Table 1. All preparations were carried out in ethanol under an atmosphere of nitrogen. With X = NCS only a type I complex was obtained, and the absorption spectrum showed no change upon adding a great excess of phosphine. With X = CN and NO₂ yellow type I complexes resulted, but solutions of these complexes turn red upon addition of trimethylphosphine. For X = CN, an approximately pure, orange red complex of type II could be isolated from dichloromethane-pentane solution. The ability of CN⁻ to stabilize 5-co-ordinated complexes of Ni(II) with higher tertiary phosphines has recently been demonstrated by Turco *et al.*³

With X = Cl, a somewhat impure dark blue compound of type II could be isolated, but it easily loses one mole of phosphine to form an ordinary red type I complex. The halides with X = Br and I, however, readily gave dark coloured complexes of type II, even when a deficiency of phosphine was used. The compounds are non-electrolytes in nitrobenzene, and mo-

Table 1. Ni(II) complexes of trimethylphosphine.

	Colour	m.p., °C ^a	Λ cm ² ·mol ⁻¹ . ohm ⁻¹ in C ₆ H ₅ NO ₂	Analyses					
				C		H		halogen/N	
				found	calc.	found	calc.	found	calc.
$[\text{Ni}(\text{NCS})_2(\text{Me}_3\text{P})_2]$	brownish red	169–170		29.30	29.39	5.64	5.55	8.62	8.57
$[\text{Ni}(\text{CN})_2(\text{Me}_3\text{P})_2]$	yellow	231–235 ^d		36.51	36.55	7.05	6.90	10.66	10.66
$[\text{Ni}(\text{NO}_2)_2(\text{Me}_3\text{P})_2]$	yellow	188–189 ^d		23.83	23.80	6.33	5.99	9.49	9.25
$[\text{NiCl}_2(\text{Me}_3\text{P})_2]$	red	199–200		25.87	25.57	6.41	6.44	25.32	25.16
$[\text{NiBr}_2(\text{Me}_3\text{P})_2]$	dark red	178–181		19.52	19.45	4.66	4.89	42.19	43.11
$[\text{Ni}(\text{CN})_2(\text{Me}_3\text{P})_3]$	orange red	165–168	0.0 (0.81) ^b	37.33	38.97	8.03	8.03	8.31	8.27
$[\text{NiBr}_2(\text{Me}_3\text{P})_3]$	blue black	140–150 ^d	0.6 (1.03)	23.89	24.19	6.14	6.09	35.94	35.76
$[\text{NiI}_2(\text{Me}_3\text{P})_3]$	violet black	160–170 ^d	0.1 (1.41)	19.98	19.99	5.24	5.03	46.77	46.94
$[\text{NiCl}(\text{Me}_3\text{P})_3]\text{ClO}_4$	red	172–176 ^d	27 (0.86)	25.35	25.62	6.48	6.45	16.58	16.81
$[\text{NiBr}(\text{Me}_3\text{P})_3]\text{ClO}_4$	red	169–170 ^d	30 (0.75)	23.32	23.18	5.76	5.84	7.33	7.60 (Cl)
								17.38	17.14 (Br)
$[\text{Ni}(\text{Me}_3\text{P})_4](\text{ClO}_4)_2$	red	explodes at ca. 190	45 (1.00) 200 ^c (1.14)	25.68	25.65	6.47	6.47	12.91	12.62
$\text{Ni}(\text{Me}_3\text{P})_4(\text{NO}_3)_2$	red	104–110 ^d	18 (0.72) 220 ^c (1.20)	29.60	29.59	8.08	7.45	5.52	5.76

^a Uncorrected. Determined in closed tubes. ^b 10³·c mol⁻¹ in brackets. ^c In water solution. ^d decomp.

molecular weight determinations (cryoscopic in benzene) show that they are monomers and only slightly dissociated to type I compounds and phosphine at 5°C. Absorption spectra in benzene or 1,2-dichloroethane are very similar to the reflectance spectra and show strong absorption bands in the 500–700 m μ region; this behaviour is characteristic of low-spin 5-co-ordinated complexes.^{4,5} The type II complexes, when boiled in 1-butanol, benzene or hexane, dissociated to type I complexes and phosphine. The dissociation $[\text{NiX}_2(\text{Me}_3\text{P})_3] \rightleftharpoons [\text{NiX}_2(\text{Me}_3\text{P})_2] + \text{Me}_3\text{P}$ is reversible, but evaporation of the boiling solutions gave the type I complex for X = Br and CN. For X = I, only impure products could be obtained. In ethanol, the type II complexes with X = Cl, Br, and I are dissociated to some degree in the manner $[\text{NiX}_2(\text{Me}_3\text{P})_3] \rightleftharpoons [\text{NiX}(\text{Me}_3\text{P})_3]^+ + \text{X}^-$ as shown by the conductivity (20–25 cm² mol⁻¹ ohm⁻¹ for 10⁻³ M solutions at 25°C) and by the fact that addition of lithium perchlorate in ethanol precipitated complexes of type III (Y = ClO₄) for X = Cl and Br.

With X = ClO₄ and NO₃, only compounds of type IV could be obtained. The perchlorate is remarkably stable and could be recrystallized from water. Infrared spectra in KBr suggest that the anions are not coordinated in the solid state; but the conductivity of the nitrate complex in nitrobenzene is lower than expected for bi-univalent electrolytes. Solutions of the nitrate complex in 1,2-dichloroethane become green upon heating, but a tetrahedral type I complex analogous to the ones formed by higher tertiary phosphines¹ has not yet been isolated. The red nitrate complex “(Me₃P)₂Ni(NO₃)₂” prepared by Beg and Clark² is presumably a mixture of Ni(Me₃P)₄(NO₃)₂ and Ni(NO₃)₂. When a great excess of trimethylphosphine is added to ethanolic nickel halide solutions, compounds of type IV apparently also are formed, as shown by a colour change to violet. The fourth phosphine, however, is very loosely bound when X = halogen, and only impure compounds could be isolated.

Experimental details, magnetic measurements and absorption spectra will be published in a future paper in this journal. We also hope to obtain X-ray structure determinations of some of the complexes.

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Corrigendum to "Crystal Structure and Alleged Isomerism of Dithiocyanate-tetrapyridine-iron(II)"*

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Table 9 page 2039 is completely in error. The correct table is as follows:

Table 9. Least squares planes through pyridine molecules. The equation of the planes can be expressed as $Px + Qy + Rz = S$ in direct space.

Ring A	Ring B
$P = -6.7641$	$P = 10.1594$
$Q = -0.1246$	$Q = 6.2620$
$R = -7.8752$	$R = -10.6651$
$S = 7.2774$	$S = -2.9476$

Distances of the atoms from the least squares planes in Å:

Ring A	Ring B
NA -0.005	NB 0.001
CA1 0.003	CB1 -0.001
CA2 0.001	CB2 -0.001
CA3 -0.003	CB3 0.003
CA4 0.001	CB4 -0.003
CA5 0.003	CB5 0.001

The standard deviations of the distances for both rings are 0.005 Å.

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