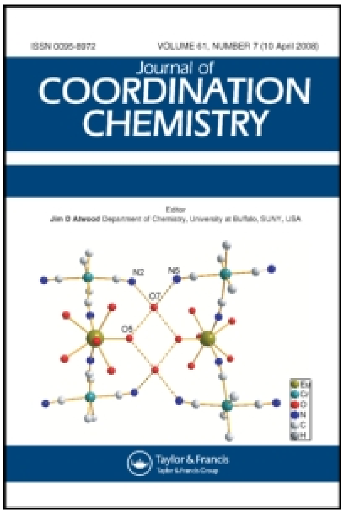

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SOME TRANSITION METAL COMPLEXES OF NOVEL DITERTIARY PHOSPHINE: [2-{Di(*p*-TOLYL)PHOSPHINO}-ETHYL] DIPHENYLPHOSPHINE

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SOME TRANSITION METAL COMPLEXES OF NOVEL DITERTIARY PHOSPHINE: [2-{Di(*p*-TOLYL)PHOSPHINO}-ETHYL] DIPHENYLPHOSPHINE

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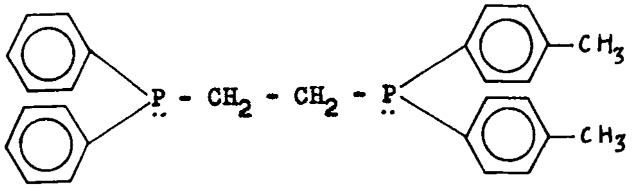
The new chelating ditertiary phosphine (pptpf) forms low spin, diamagnetic, square-planar complexes of the type [M(pptpf)X_2] (where M = Ni(II), Pd(II) or Pt(II); X = Cl, Br, I or NCS) when treated with corresponding metal salts. Group VI metal hexacarbonyls also react with the ligand (pptpf) to yield diamagnetic, octahedral complexes of type [M$(CO)_4$(pptpf)] (where M = Cr, Mo or W). These complexes have been characterised on the basis of their elemental analysis, ^{1}H n.m.r., electronic, infrared spectral measurements, electrical conductance and magnetic susceptibilities data. In all the complexes the ligand (pptpf) acts as a chelating ditertiary phosphine.

INTRODUCTION

During the last few years, metal complexes of ditertiary phosphines have been extensively studied.[1] It has been shown that the properly substituted organic groups on phosphorus atoms in ditertiary phosphine ligand can increase the solubility characteristic of the metal complexes.[2] In view of the above, it was considered worthwhile to synthesize new ditertiary phosphine metal complexes having better solubility characteristics in order to study their catalytic behaviour.

In this paper we describe the preparation and characterization of a new ligand, [2-{di(*p*-tolyl)-phosphino}ethyl] diphenylphosphine (pptpf) (Figure 1). We also describe its reactions with different metals.



(pptpt)

FIGURE 1

EXPERIMENTAL

Chemicals used were of Analytical Grade. Solvents were dried and purified by Standard methods.[3] The solvents were degassed before use. Nitromethane (B.D.H., A.R.) was washed with 5% aqueous sulphuric acid and 5% sodium bicarbonate solutions, and fractionally distilled, with the middle fraction boiling at 101°C being employed.

All the reactions were carried out under nitrogen. Carbon and hydrogen were estimated by the combustion methods, phosphorus was determined as ammonium phosphomolybdate and nickel as dimethylglyoximate. The ^{1}H n.m.r. spectra were recorded in $CDCl_3$ solutions on Varian A-60 spectrometer. The molar conductances were determined on a Elico conductivity bridge CM 82 T. Magnetic susceptibilities were measured by the Gouy method. Infrared spectra in KBr pellets were recorded on a Perkin-Elmer 621 spectrophotometer. The electronic spectra were determined in nujol and acetone and were run on a Russian ϕ10 spectrophotometer.

SYNTHESIS OF LIGANDS

The ligand, [2-{di(*p*-tolyl)phosphino}ethyl]diphenylphosphine (pptpf) was prepared by the reaction of diphenylvinylphosphine and di(*p*-tolyl)phosphine in the presence of potassium tertiary butoxide,[4] as described below.

A mixture of 21.2 g (100 mole) of diphenylvinylphosphine, 21.4 g (100 mmol) of di-p-tolylphosphine and 0.6 g (5.96 mmol) of potassium tertiary butoxide and 200 ml of $LiAlH_4$ dried tetrahydrofuran was refluxed for 6 hrs. After the reaction was over, the tetrahydrofuran was removed under reduced pressure leaving behind a pale yellow solid. It was washed five times with methanol and dried to give 34.9 g (82% yield) of $(C_6H_5)_2PCH_2CH_2P(p\text{-}CH_3C_6H_4)_2$. After two crystallizations from a mixture of benzene and methanol 29.8 g (70% yield) of pure $(C_6H_5)_2PCH_2CH_2P(p\text{-}CH_3C_6H_4)_2$ m.p. 81–82° was obtained. (Found: C. 78.7; H. 6.45; P. 14.35; calc. for $C_{28}H_{28}P_2$: C. 78.86; H. 6.61; P. 14.53%).

PREPARATION OF COMPLEXES

Dichloro[2-{di(p-tolyl)phosphino}ethyl]diphenylphosphine nickel(II)

$NiCl_2 \cdot 6H_2O$ (0.237 g, 1.0 mmol) was dissolved in butan-1-ol (40 ml). On refluxing for 2 h a light green solution was obtained. To this was added [2-{di(p-tolyl)phosphino}ethyl]diphenylphosphine (0.426 g, 1.0 mmol) which produced a deep red solution. It was refluxed for 2 hrs. On cooling, red crystals were deposited, which were collected on a sintered-glass funnel and crystallized from methylene chloride/n-hexane.

Dibromo[2-{di(p-tolyl)phosphino}ethyl]diphenylphosphine nickel(II)

This complex was prepared as above using $NiBr_2$. The crude product was crystallized by methylene chloride/n-hexane or methylene chloride/ethanol to give brown crystals.

Diiodo[2-{di(p-tolyl)phosphino}ethyl]diphenylphosphine nickel(II)

A solution of NiI_2 was freshly prepared by refluxing $Ni(NO_3)_2 \cdot 6H_2O$ (0.580 g, 2.0 mmol) and KI (1 g, 6 mmol) in butan-1-ol (40 ml) for 2 h. The resulting mixture was cooled and filtered. The filtrate was refluxed for 1 h and to this [2-{di(p-tolyl)phosphino}ethyl]diphenylphosphine (0.63 g, 1.5 mmol) was added. The solution became mauve in colour. On cooling, mauve coloured crystals were deposited, which were collected and crystallized in the same manner as the bromide.

Dithiocyanato[2-{di(p-tolyl)phosphino}ethyl]diphenylphosphine nickel(II)

A solution of $Ni(NCS)_2$ was freshly prepared as described for the iodide from $Ni(NO_3)_2 \cdot 6H_2O$ (0.580 g, 2 mmol), KSCN (0.580 g, 6 mmol) and butan-1-ol (30 ml). The complex was prepared in the same manner as the iodo analogue.

Diperchlorato di[2-{di(p-tolyl)phosphino}ethyl]diphenylphosphine nickel(II)

$Ni(ClO_4)_2 \cdot 6H_2O$ (0.370 g, 1.0 mmol) dissolved in butan-1-ol (40 ml) was refluxed (2 h) to produce a green solution. To this solution the ligand (pptpf) (0.853 g, 2.0 mmol) was added, producing a yellow solution. It was refluxed for 2 h. On cooling, yellow crystals were deposited, which were collected and dried under vacuum.

Dichloro[2-{di(p-tolyl)phosphino}ethyl]diphenylphosphine palladium(II)

Palladium dichloride (0.355 g, 2.0 mmol) dissolved in acetonitrile (50 ml) was refluxed (1 h) to produce a brown solution. To this solution (pptpf) (0.853 g, 2.0 mmol) was added and the mixture was refluxed for a further 3 h. A grey product was obtained, which was filtered and purified by treating with charcoal in refluxing methylene chloride.

Dibromo, diiodo and dithiocyanato[2-{di(p-tolyl)phosphino}ethyl]diphenylphosphine palladium(II)

These complexes were prepared by treating the dichloro-[2-{di(p-tolyl)phosphino}ethyl]diphenylphosphine palladium (II) complex with an excess of the corresponding potassium salt or ammonium thiocyanate in boiling acetone. The resulting mixture was filtered and dried. The complexes were extracted with methylene chloride.

Dichloro[2-{di(p-tolyl)phosphino}ethyl]diphenylphosphine platinum(II)

Potassium tetrachloroplatinate (0.830 g, 2.0 mmol) dissolved in ethanol was treated with ligand (pptpf) (0.853 g, 2.0 mmol) in methylene chloride. A black precipitate formed immediately; it was filtered and washed with water. The solid so obtained was heated with equal volumes of concentrated HCl and ethanol under reflux for 4 h where upon a white complex was formed. The residue was separated, washed with ethanol and dried under vacuum to give the pure white complex.

Dibromo and diiodo[2-{di(p-tolyl)phosphino}ethyl]-diphenylphosphine platinum(II)

These complexes were prepared similarly to the procedure adopted for the corresponding palladium complexes.

[2-{Di(p-tolyl)phosphino}ethyl]diphenylphosphine tetracarbonyl chromium(O)

A mixture of $Cr(CO)_6$ (0.220 g, 1.0 mmol) and ligand (pptpf) (0.426 g, 1.0 mmol) was boiled under reflux for 30 hr in 50 ml of methylcyclohexane. After cooling to room temperature, solvent was removed from the reaction mixture 25°/0.1 mm. The crude product was recrystallized from the mixture of benzene and *n*-hexane to give yellow crystalline complex.

[2-{Di(p-tolyl)phosphino}ethyl]diphenylphosphine tetracarbonyl molybdenum(O)

A mixture of $Mo(CO)_6$ (0.264 g, 1.0 mmol) and ligand (pptpf) (0.426 g, 1.0 mmol) was boiled under reflux for 30–40 h in 50 ml of methylcyclohexane. After cooling to room temperature, solvent was removed from the reaction mixture under pressure to give yellow product, which was crystallized from the mixture of benzene and *n*-hexane.

[2-{Di(p-tolyl)phosphino}ethyl]diphenylphosphine tetracarbonyl tungsten(O)

A mixture of $W(CO)_6$ (0.35 g, 1.0 mmol) and ligand (pptpf) (0.426 g, 1.0 mmol) was boiled under reflux for 60 h in 50 ml of methylcyclohexane. After cooling to room temperature, solvent was removed from the reaction mixture under pressure to give white product, which was crystallized from the mixture of benzene and *n*-hexane.

RESULTS AND DISCUSSION

Metal Halide Complexes

Complexes of nickel(II) having general formula $[Ni(pptpf)X_2]$ (X = Cl, Br, I or NCS) (Table II) formed immediately by mixing nickel(II) salt with ligand (pptpf) in 1 : 1 molar ratio in butan-1-ol. Stable chloro complexes of palladium(II) and platinum(II) were prepared by reaction of ligand (pptpf) with palladium dichloride and potassium tetrachloroplatinate, respectively. The corresponding bromo, iodo and thiocyanato complexes were easily prepared by metathetical exchange reactions.

Nickel(II), palladium(II) and platinum(II) halide complexes of ligand (pptpf) are soluble in chloroform, dichloromethane and acetone but are insoluble in hexane and petro–ether (60–80°C). Similarly, chromium, molybdenum and tungsten carbonyl complexes of ligand (pptpf) (Table II) are also soluble in benzene and chloroform but are insoluble in petro–ether (60–80°C). However, on comparison of the solubility of these metal complexes of [2-{di(*p*-tolyl)-phosphino}ethyl]diphenylphosphine with those of extensively studied[11] ditertiary phosphine, 1,2-bis-diphenylphosphinoethane, it appears that complexes of ligand (pptpf) are more soluble than that of the corresponding 1,2-bisdiphenylphosphinoethane complexes. Rest of the chemistry of (pptpf) complexes is more of less similar to the 1,2-bisdiphenylphosphinoethane complexes.

TABLE I

^1H n.m.r. and i.r. data of [2-{di(*p*-tolyl)phosphino}ethyl]-diphenylphosphine.

^1H n.m.r. chemical shifts

δ[ppm]	Multiplicity	Origin	Solvent/Reference
7.7–7.25	Multiplet	arom. protons	$CdCl_3$/TMS
2.4	Singlet	$—CH_3$	
2.2–2.05	Triplet	$—P—CH_2—$	

I.r. frequencies (KBr pellet): 3040(b), 2900(w), 1595(w), 1580(w), 1495(w), 1480(m), 1430(s), 1390(w), 1305(w), 1270(w), 1185(m), 1160(s), 1090(s), 1060(m), 1025(m), 995(vw), 805(s), 750(s), 730(s), 695(s), 675(w), 615(w), 510(s), 500(s), 460(m), 440(s), 395(vw), 335(w).

s = strong, b = broad, w = weak, v = very, m = medium.

The infrared spectra of $[M(pptpf)X_2]$ (where M = Ni(II), Pd(II) or Pt(II); X = Cl, Br, I or NCS) are very similar to the free ligand spectra (Table I), the most important change being an appearance of band at ~1100 cm^{-1}. This band is more intense than ligand band occurring due to *p*-phenyl grouping at ~1090 cm^{-1}, which indicates the coordination of phosphorus to metal[5] (Figure 2).

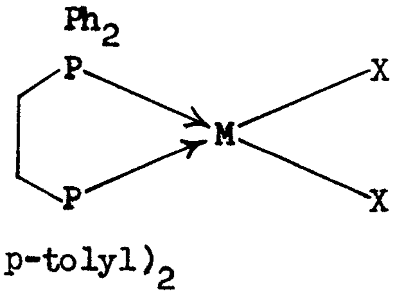


FIGURE 2 Where M = Ni(II), Pd(II) or Pt(II); X = Cl, Br, I or NCS.

TABLE II
Analytical data of transition metal complexes of [2-{di(*p*-tolyl)phosphino}ethyl]diphenylphosphine (pptpf).

Compound	Found %				Required %			
	C	H	P	M	C	H	P	M
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
[Ni(pptpf)Cl_2]	59.9	4.8	10.8	10.2	60.4	5.1	11.1	10.5
[Ni(pptpf)Br_2]	51.8	4.0	9.2	9.0	52.1	4.3	9.6	9.1
[Ni(pptpf)I_2]	44.8	3.7	8.2	7.6	45.4	4.8	8.4	7.8
[Ni(pptpf)$(NCS)_2$]	59.5	4.5	9.3	9.3	59.9	4.7	9.7	9.6
[Ni$(pptpf)_2$]$(ClO_4)_2$	48.9	3.8	8.75	8.1	49.2	4.1	9.1	8.0
[Pd(pptpf)Cl_2]	49.7	4.55	9.8	—	50.1	4.7	10.3	—
[Pd(pptpf)Br_2]	48.25	3.6	8.65	—	48.5	4.0	8.3	—
[Pd(pptpf)I_2]	42.4	3.45	7.6	—	42.7	3.6	7.9	—
[Pd(pptpf)$(NCS)_2$[	55.2	4.1	9.15	—	55.5	4.3	9.4	—
[Pt(pptpf)Cl_2]	48.3	3.75	8.8	—	48.5	4.0	9.0	—
[Pt(pptpf)Br_2]	42.7	3.4	7.4	—	43.0	3.6	7.9	—
[Pt(pptpf)I_2]	38.1	3.0	6.8	—	38.4	3.2	7.2	—
[(pptpf)Cr$(CO)_4$]	64.8	4.7	10.3	—	65.0	4.8	10.5	—
[(pptpf)Mo$(CO)_4$]	60.25	4.2	9.75	—	60.6	4.4	9.8	—
[(pptpf)W$(CO)_4$]	53.0	3.0	8.3	—	53.2	3.1	8.6	—

For the metal-thiocyanate-phosphine complexes, two ν(C—N) absorptions, separated by <20 cm^{-1} are expected for *cis*-[ML_2X_2] complexes. The characteristic absorption due to N-bonded thiocyanate occurs at below 2100 cm^{-1} whereas absorption occurs above 2100 cm^{-1} for S-bonded thiocyanate.[6] Moreover, ν(C—N) is broad, whereas for M—SCN, it is sharp. In the case of [Ni(pptpf)$(NCS)_2$] and [Pd(pptpf)$(NCS)_2$] complexes, peaks at 2080 cm^{-1} and 2040 cm^{-1}, respectively, were observed due to ν(C—N) absorptions, that is indicative of an N-bonded thiocyanate group.[7,8] By comparing the spectra of [M(pptpf)-$(NCS)_2$] (M = Ni(II) or Pd(II) with that of free ligand and bromo complex spectra, two addition vibrations of the isothiocyanate group (M—N—C—S) were observed due to ν(C—S) at 850 cm^{-1} and $\delta_{(NCS)}$ at 475 cm^{-1} in nickel(II) and $\nu_{(C-S)}$ at 860 cm^{-1}, $\delta_{(NCS)}$ at 470 cm^{-1} in palladium complexes.

The infrared spectra of the complex [Ni$(pptpf)_2$] $(ClO_4)_2$ exhibits bands at 1105 and 625 cm^{-1} associated with the perchlorate anions. These bands are not split, and confirms that the perchlorate groups are ionic and not coordinated.[9]

The infrared spectra (400–200 cm^{-1}) of complexes [M(pptpf)X_2] (M = Ni(II), Pd(II) or Pt(II); X = Cl, Br, I or NCS) were studied. The stretching vibrations due to $\nu_{(M-X)}$ were at 325, 340 cm^{-1} for $\nu_{(Ni-Cl)}$, 265, 290 cm^{-1}, for $\nu_{(Ni-Br)}$, 285, 210 cm^{-1} for $\nu_{(Pd-Cl)}$, 240 cm^{-1} for $\nu_{(Pd-Br)}$ 285, 315 cm^{-1} for $\nu_{(Pt-Cl)}$, and 220, 280 cm^{-1} for $\nu_{(Pt-Br)}$ and have been assigned by comparison with the corresponding iodo complexes. Bands resulting from Ni—NCS and Pd—NCS are usually strong and found at 330 cm^{-1} and 320 cm^{-1}, respectively.

All these complexes [M(pptpf)X_2] (M = Ni(II), Pd(II), or Pt(II); X = Cl, Br, I or NCS) are diamagnetic and non-electrolytes in acetone solutions, whereas [Ni$(pptpf)_2$] $(ClO_4)_2$ is diamagnetic but behaves as 1 : 2 electrolyte in nitromethane (Table III).

The electronic spectra of complexes [Ni(pptpf)X_2] (X = Cl, Br, I or NCS) have been carried out in nujol

TABLE III
Some physical properties of transition metal complexes of [2-{di(*p*-tolyl)phosphino}ethyl]diphenylphosphine (pptpf).

Compound	Colour	M.p.(°C)	ΔM	μ_{eff}
[Ni(pptpf)Cl_2]	Red	255–256	4	0.4
[Ni(pptpf)Br_2]	brown	295	7	0.4
[Ni(pptpf)I_2]	mauve	259	6	0.3
[Ni(pptpf)$(NCS)_2$]	yellow	335	0	0.3
[Ni$(pptpf)_2$]$(ClO_4)_2$	yellow	258	182[a]	0.4
[Pd(pptpf)Cl_2]	white	285	8	0.1
[Pd(pptpf)Br_2]	yellow	320–321	10	0.3
[Pd(pptpf)I_2]	yellow	284	6	0.2
[Pd(pptpf)$(NCS)_2$]	light yellow	215	5	0.4
[Pt(pptpf)Cl_2]	white	314	0	0.3
[Pt(pptpf)Br_2]	yellow	245–246	7	0.3
[Pt(pptpf)I_2]	yellow	273	5	0.3
[(pptpf)Cr$(CO)_4$]	yellow	118–119	—	—
[(pptpf)Mo$(CO)_4$]	yellow	132	—	—
[(pptpf)W$(CO)_4$]	white	165	—	—

ΔM in δ cm^2 mole^{-1} for c. 10^3 M acetone solutions at 25°C.
[a] In nitromethane.

and acetone solution (Table IV). Venanzi *et al.*[10] indicate that square-planar diphosphine nickel dihalide has bands in the region 450–500 nm, whereas tetrahedral complexes have bands in the near-infrared region. In the case of [Ni(pptpf)X_2] (X = Cl, Br, I or NCS) an intense absorption in the 400–500 nm region was observed, and this absorption refers to the transition which has *d*-orbital character $d_{xy} \rightarrow d_{x^2-y^2}$, which confirms the square-planar configuration of the complexes (Figure 2). This band moves to higher energy in the series $I^- < Br^- < Cl^- < NCS^-$ and it is found that the extinction coefficient of these bands increases in parallel order.

TABLE IV
Electronic spectra (nm) of dihalogeno and dithio-cyanato complexes of nickel(II) with [2-{di(*p*-tolyl)phosphino}ethyl]-diphenylphosphine (pptpf).

S. No.	Compound	λ_{max} (ϵ) in acetone	in nujol
1.	[Ni(pptpf)Cl_2]	478 (1530)	475 (1525)
2.	[Ni(pptpf)Br_2]	490 (1510)	490 (1525)
3.	[Ni(pptpf)I_2]	495 (1050)	500 (1055)
4.	[Ni(pptpf)$(NCS)_2$]	450 (1650)	440 (1640)

Metal Carbonyl Complexes

The complexes with group VI metal hexacarbonyls [(pptpf)M$(CO)_4$] (M = Cr, Mo or W) were easily prepared as described above.

The infrared spectra of metal carbonyl complexes of [2-{di(*p*-tolyl)phosphino}ethyl]diphenylphosphine indicates an increase in intensity and frequency ~10–15 cm^{-1} of the band 1090 cm^{-1}, occurring due to ν(P—Ph) in the free ligand, which refers to the coordination of phosphorus to metal[5] (Figure 3).

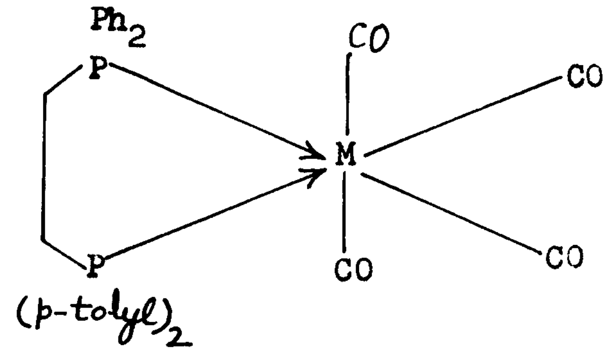


FIGURE 3 Where M = Cr, Mo or W.

The four $\nu_{(CO)}$ bands were observed in [(pptpf)M$(CO)_4$] (M = Cr, Mo or W) complexes. These $\nu_{(CO)}$ frequencies, when compared to the analogous ditertiary phosphine (pmtpf) [2-{di(*m*-tolyl)phosphino}ethyl]diphenylphosphine metal carbonyl complexes, were found almost identical (Table V).

¹H n.m.r. spectra

The proton n.m.r. spectra of the free ligand (pptpf) (Figure 1) are given in Table I. In ¹H n.m.r. spectra of complexes [M(pptpf)X_2] (where M = Ni(II), Pd(II) or Pt(II); X = Cl, Br, I or NCS) and [M(pptpf)M$(CO)_4$] (M = Cr, Mo or W), was observed, slightly downfield shift of the aromatic (at δ 7.8–7.35) and methyl resonance (at δ 2.6–2.3), compared to those of free ligands.

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TABLE V
$\nu_{(CO)}$ frequencies of chelating ditertiary phosphine complex of metal carbonyls.

S. No.	Compound	Medium	$\nu_{(CO)}$ (cm^{-1})	Reference
1.	[(pptpf)Cr$(CO)_4$]	KBr	2030, 1898, 1890, 1855	*a*
2.	[(pmtpf)Cr$(CO)_4$]	C_6H_6	2008, 1914, 1898, 1876	*b*
3.	[(pptpf)Mo$(CO)_4$]	KBr	2010, 1910, 1855, 1840	*a*
4.	[(pmtpf)Mo$(CO)_4$]	C_6H_6	2020, 1917, 1906, 1879	*b*
5.	[(pptpf)W$(CO)_4$]	KBr	2005, 1930, 1910, 1880	*a*
6.	[(pmtpf)W$(CO)_4$]	C_6H_6	2014, 1910, 1900, 1877	*b*

pptpf = [2-{di(*p*-tolyl)phosphino}ethyl]diphenylphosphine.
pmtpf = [2-{di(*m*-tolyl)phosphino}ethyl]diphenylphosphine.
[a] – this work.
[b] – N. D. Sadanani, A. Walia, P. N. Kapoor and R. N. Kapoor, *Aust. J. Chem.* **32**, 1143 (1979).

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