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Organometallic chemistry of diphosphazanes

IV *. Reactions of the cyclodiphosphazane, *cis*-[^{t}BuNP(OPh)]$_2$ with M(CO)$_6$ (M = Cr, Mo, W), rhodium(I), palladium(II) and platinum(II) derivatives

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Abstract

The reactions of the cyclodiphosphazane, *cis*-[^{t}BuNP(OPh)]$_2$(L) with M(CO)$_6$ (M = Cr, Mo or W) as well as Pd^{II} and Pt^{II} derivatives afford mononuclear complexes of the type [M(CO)$_4$L$_2$] (M = Cr, Mo or W) and [MCl$_2$L$_2$] (M = Pt or Pd) in which the cyclodiphosphazane acts as a monodentate ligand. Reactions with Rh^I derivatives yield the complexes [Rh(COD)LCl] (COD = 1,5-cyclooctadiene) and [RhCl(CO)(μ-L)]$_2$ in which the cyclodiphosphazane exhibits monodentate and bridged-bidentate modes of coordination, respectively. The structures of the complexes have been deduced mainly from ^{31}P NMR spectroscopic data.

Introduction

The coordination chemistry of four-membered cyclodiphosphazanes, (RNPX)$_2$ has been studied [1-3] to a lesser extent than that of their acyclic analogues, X$_2$PN(R)PX$_2$ [4,5]. Cyclodiphosphazanes exhibit different coordination behaviour in their transition metal complexes [2a]. Nixon and coworkers have reported synthetic, spectroscopic and structural studies of platinum(II), palladium(II), and rhodium(I) derivatives in which both monodentate and bridged bidentate modes of coordination of cyclodiphosphazanes are observed [2]. Scherer et al. [3] have reported the synthesis of platinum(0) complexes containing monodentate methyl-substituted cyclodiphosphazanes and a dirhenium complex, [Re$_2$(μ-Br)$_2$(CO)$_6${μ-(^{t}BuNPMe)$_2$}], in which the cyclodiphosphazane bridges the two rhenium metal centres.

We are interested in the coordination chemistry of fluoroalkoxy or aryloxy substituted diphosphazanes as these substituents would confer increased thermal

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and hydrolytic stability on these ligands relative to the halogeno derivatives and also enhance their π-acidic character [4]. We report here the syntheses and spectroscopic studies of group 6 metal carbonyl, rhodium(I), palladium(II) and platinum(II) complexes of the phenoxy-substituted cyclodiphosphazane, *cis*-(^{t}BuNP(OPh))$_2$.

Experimental

All manipulations were carried out under dinitrogen by standard Schlenk line techniques [6]. Solvents were distilled under dinitrogen and degassed prior to use. The light petroleum used was the fraction of b.p. 60–80°C. Metal hexacarbonyls M(CO)$_6$ (M = Cr, Mo, W) were purchased from Strem Chemicals. [Mo(CO)$_4$(NBD)] (NBD = norbornadiene) [7], [Mo(CO)$_4$(pip)$_2$] (pip = piperidine) [8], [MCl$_2$(COD)] (M = Pd, Pt) [9], [PdCl$_2$(NCPh)$_2$] [10], [RhCl(COD)]$_2$ [11] and [RhCl(CO)$_2$]$_2$ [12] were prepared by published procedures.

NMR and IR spectroscopic measurements were carried out as described previously [4a]. Elemental analyses were carried out at City University, London, UK through the kind offices of Dr. S.A. Matlin.

Preparation of [^{t}BuNP(OPh)]$_2$ (1)

A solution of [^{t}BuNPCl]$_2$ [2b] (15 mmol) in 75 ml of benzene was added dropwise to a suspension of sodium phenoxide (prepared *in situ* from phenol (30 mmol) and sodium (30 mmol) in benzene (100 mL), at 10°C. The mixture was stirred for 3 h and filtered. The solvent was evaporated from the filtrate under vacuum to leave *cis*-[^{t}BuNP(OPh)]$_2$ (**1**), which was recrystallized from a mixture of CH_2Cl_2 and light petroleum (1/3). Yield: 70%. M.p.: 47–49°C. ^{1}H NMR (CDCl$_3$): 1.38 (s, ^{t}Bu), 7.20 (m, OPh). ^{31}P NMR (CHCl$_3$): 143.3 (s). Anal. Found: C, 61.5; H, 7.1; N, 7.1. $C_{20}H_{28}N_2O_2P_2$ calcd.: C, 61.5; H, 7.1; N, 7.1%.

The same procedure was used to prepare the *p*-bromophenoxy derivative, (^{t}BuNP(OC$_6$H$_4$Br-*p*))$_2$ [13].

Preparation of cis-*[M(CO)$_4${(^{t}BuNP(OPh))$_2$}$_2$] [M = Cr (3), Mo (4) or W (6)]*

Anhydrous Me$_3$NO (1.00 or 2.00 mmol) was added at 0°C with vigorous stirring to a solution of M(CO)$_6$ (1.0 mmol) in 20 mL of dry acetonitrile. After 30 min, the clear solution was warmed to 25°C and a solution of (^{t}BuNP(OPh))$_2$ in acetonitrile was added dropwise with vigorous stirring. Stirring was continued for 2 h and the mixture then filtered through Celite. Concentration of the filtrate under reduced pressure followed by the addition of methanol gave the title compounds in 48–62% yield.

The molybdenum complex **4** was also prepared in 65% yield by the reaction of **1** with [Mo(CO)$_4$(NBD)] in hexane or [M(CO)$_4$(pip)$_2$] in dichloromethane.

Preparation of [RhCl(COD)(^{t}BuNP(OPh))$_2$] (7)

A solution of [^{t}BuNP(OPh)]$_2$ (0.158 g, 0.40 mmol) in benzene (10 mL) was added dropwise to a stirred solution of [RhCl(COD)]$_2$ (0.100 g, 0.20 mmol) in benzene (20 mL) under nitrogen. After 30 min, the solvent was removed under reduced pressure and the oily residue was washed with 50 mL of diethyl ether to

Table 1

Analytical and IR spectroscopic data for cyclodiphosphazane complexes **3–10**

Compound [a]	Colour/M.p. (°C)	IR [b] ν(CO) (cm^{-1})	Elemental analyses (Found (calcd.) (%))		
			C	H	N
$[Cr(CO)_4(L)_2]$	pale green/142–144	2040, 1960, 1930, 1890	56.8	5.4	4.1
3			(55.9)	(5.9)	(5.9)
$[Mo(CO)_4(L)_2]$	white/138–139	2060, 1965, 1915, 1895	52.8	5.8	5.6
4			(53.4)	(5.7)	(5.7)
$[Mo(CO)_4L'_2]$	white/168 (dec)	2060, 2000–1900 br	40.1	3.8	4.0
5			(40.4)	(4.1)	(4.3)
$[W(CO)_4L_2]$	pale yellow/165–166	2010, 1935, 1895, 1880	48.6	5.1	4.6
6			(49.1)	(5.2)	(5.2)
[RhCl(COD)L]	yellow/114 (dec)	–	52.2	6.0	4.1
7			(52.1)	(5.4)	(3.8)
$[RhCl(CO)L]_2$	yellow/93	2020	48.2	5.8	4.7
8 [c]			(48.3)	(5.4)	(4.8)
cis-$[PdCl_2L_2]$	yellow/190 (dec)	298, 315 [e]	46.5	5.6	5.6
9a [d]			(47.2)	(5.6)	(5.4)
trans-$[PdCl_2L_2]$	yellow/183–185	347, 355 [e]	50.1	6.0	5.6
9b			(50.1)	(5.8)	(5.8)
cis-$[PtCl_2L_2]$	white/148 (dec)	284, 302 [e]	43.6	5.3	3.7
10 [d]			(43.5)	(5.1)	(5.0)

[a] L = [^{t}BuNP(OPh)]$_2$; L′ = [^{t}BuNP(OC$_6$H$_4$Br-*p*)]$_2$. [b] **3–8** in nujol mull, **9a**, **9b** and **10** in polyethylene pellet. [c] Isolated as benzene solvate **8** C$_6$H$_6$; molecular mass in benzene (vapour phase osmometry) 960 daltons. [d] Isolated as solvates containing one molecule of CH$_2$Cl$_2$. [e] ν(M–Cl)

give **7** as a yellow solid (yield 68%). An analytically pure sample was obtained by recrystallization from a mixture of CH_2Cl_2 and light petroleum (1/2).

Preparation of $[RhCl(CO)(^tBuNP(OPh))_2]_2$ *(8)*

A solution of $[^tBuNP(OPh)]_2$ (0.20 g, 0.50 mmol) in benzene (10 mL) was added dropwise with stirring to a solution of $[RhCl(CO)_2]_2$ (0.1 g, 0.25 mmol) in the same solvent (20 mL). Stirring was continued for 1 h. Concentration of the resulting solution under reduced pressure followed by the addition of *n*-hexane gave a bright-yellow precipitate of **8** which was filtered off, washed with *n*-hexane, and recrystallized from a mixture of benzene and light petroleum (1/2) to give an analytically pure sample (87% yield).

Reactions of $[^tBuNP(OPh)]_2$ *with* cis-$[PdCl_2(COD)]$ *and* trans-$[PdCl_2(NCPh)_2]$

A mixture of *cis*-$[PdCl_2(COD)]$ (0.2 g, 0.70 mmol) and $[^tBuNP(OPh)]_2$ (0.55 g, 1.40 mmol) in 30 mL of CH_2Cl_2 was stirred at 30°C for 30 min. The solution was filtered, the filtrate concentrated to 5 mL, and light petroleum (50 mL) added to give *cis*- and *trans*-isomers of $[PdCl_2\{(^tBuNP(OPh))_2\}_2]$ in 72% yield.

Reaction of $[^tBuNP(OPh)]_2$ with *trans*-$[PdCl_2(NCPh)_2]$ in 2:1 molar ratio under similar conditions gave the pure *trans*-isomer (**9b**) in 75% yield.

Preparation of cis-$[PtCl_2\{(^tBuNP(OPh))_2\}_2]$ *(10)*

A solution of $[PtCl_2(COD)]$ (0.247 g, 0.66 mmol) and $[^tBuNP(OPh)]_2$ (0.52 g, 1.32 mmol) in dichloromethane (25 ml) was heated under reflux with stirring for 3 h. The solution was cooled to room temperature and filtered through Celite. The filtrate was concentrated to 5 mL and light petroleum (50 mL) was added to produce a colourless precipitate of $[PtCl_2\{(^tBuNP(OPh))_2\}_2]$ (70% yield). An

Table 2

NMR data for the cyclodiphosphazane complexes **3–10**

Compound	^{31}P [a]			^1H [b]
	P_u	P_c	coupling constants (Hz)	
3	128.4 d	181.8 d	$^2J(PP) = 10$	1.50 s
4 [e]	130.0 s	151.0 s		1.50 s
5	129.0 s	152.0 s		1.46 s
6	127.1 s	114.8 s	[c]	1.50 s
7 [d]	128.6 d	107.5 d	$^1J(RhP) = 231.2$, $^2J(PP) = 24.1$	1.60 s
8	–	120.0 d	$^1J(RhP) = 158.6$	1.45 s
9a	127.7 t	78.8 t		1.55 s
9b	128.6 t	84.5 t		1.47 s
10	125.8 dd	44.5 dd	$^1J(PtP) = 4835$, $^2J(PP) = 7.6$ $^3J(PtP) = 22.7$ Hz	1.51 s

[a] **4–7** in CH_2Cl_2 and **3**, **8** and **9** in $CDCl_3$ solution at 32.2 MHz, **10** in $CDCl_3$ solution at 101.5 MHz, P_u uncoordinated phosphorus, P_c coordinated phosphorus, d doublet, t triplet [b] In $CDCl_3$ solution at 60 MHz, data given only for tert-butyl protons, δ of phenyl protons omitted, s singlet, m multiplet [c] P–P coupling is too small to be observed [d] The protons of C_8H_{12} appears as multiplets at δ 2.2 and 4.1 [e] $^1J(WP)$ could not be observed owing to poor signal-to-noise ratio

analytically pure sample was obtained by recrystallization from a mixture of CH_2Cl_2 and light petroleum (1/2).

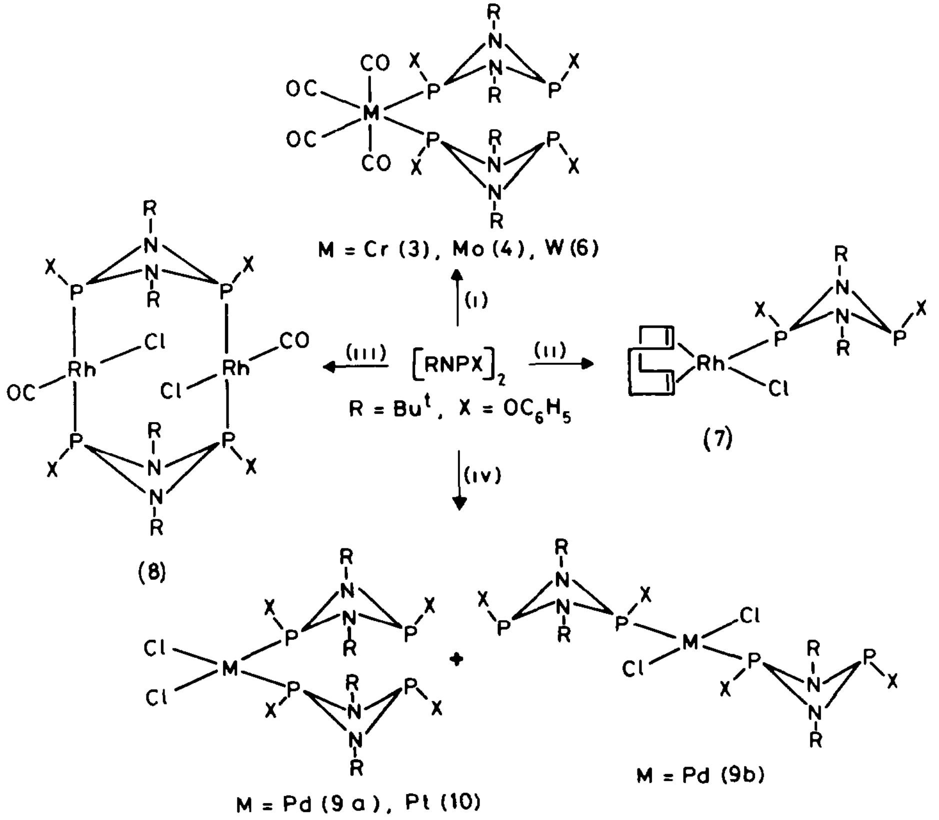
Analytical and spectroscopic data for the cyclodiphosphazane complexes are given in Tables 1 and 2.

Results and discussion

Reactions of [^{t}BuNP(OPh)]$_2$ (1) with group 6 metal carbonyl derivatives

The reactions of *cis*-[^{t}BuNP(OPh)]$_2$ (**1**) with various metal derivatives are summarised in Scheme 1.

Two approaches were used for the synthesis of cyclodiphosphazane complexes of Group 6 metal carbonyls (Scheme 1). Reactions of *cis*-[^{t}BuNP(OPh)]$_2$ (**1**) with either [Mo(CO)$_4$(NBD)] or [Mo(CO)$_4$(pip)$_2$] under refluxing conditions gave *cis*-[Mo(CO)$_4$\{(^{t}BuNP(OPh))$_2$\}$_2$] (**4**) in which cyclodiphosphazane ligands are coordinated to the metal in the η^1-fashion. In the case of the *p*-bromophenoxy ligand [^{t}BuNP(OC$_6$H$_4$Br-*p*)]$_2$, only the molybdenum complex, *cis*-[Mo(CO)$_4$\{(^{t}BuNP(OR))$_2$\}$_2$] (R = C$_6$H$_4$Br-*p*) (**5**) was obtained. When [^{t}BuNP(OPh)]$_2$ was treated with M(CO)$_6$ (M = Cr, Mo or W) in the presence of an equimolar amount of



Scheme 1. Reactions of [^{t}BuNP(OPh)]$_2$ with various transition metal derivatives: (i) [Mo(CO)$_4$(pip)$_2$], [Mo(CO)$_4$(NBD)] or [M(CO)$_6$]/Me$_3$NO; (ii) [RhCl(COD)]$_2$; (iii) [RhCl(CO)$_2$]$_2$ and (iv) [M(COD)Cl$_2$]

Me_3NO, the same type of complex (**3**–**6**) was obtained. In both the approaches, the reactions were carried out with various molar ratios of the reactants and under a variety of conditions. In all cases only the *cis*-complexes were formed.

Complexes **3**–**6** are the first examples of group 6 tetracarbonyl derivatives of cyclodiphosphazanes in which cyclodiphosphazanes exhibit monodentate coordination. Zeiss and Feldt [1a] and also Maisch [1b,1c] have reported only pentacarbonyl complexes of the type, $[M(CO)_5(RNPX)_2]$ and $[\{M(CO)_5\}_2(RNPX)_2]$ in which cyclodiphosphazanes exhibit monodentate and bridged bidentate modes of coordination. Nixon and coworkers [2a] have pointed out that the reactions of $(^tBuNPX)_2$ (X = F, Cl) with Group 6 metal carbonyl derivatives give a mixture of products. Norman and coworkers [16] have reported that the reactions of $(PhNPX)_2$ (X = Cl, NHPh) with *cis*-$[Mo(CO)_4(NBD)]$ result in a mixture of products, as revealed by the complex ^{31}P NMR spectrum, the resonances of which could not be assigned. However, in the present study the complexes **3**–**6** were isolated as microcrystalline solids. The ^{31}P NMR spectra of the molybdenum and chromium complexes reveal the presence of a trace impurity that could not be identified.

The IR spectra of complexes **3**–**6** exhibit four strong $\nu(CO)$ frequencies in the range 2060–1840 cm^{-1} (see Table 1), characteristic of tetracarbonyl diphosphazane complexes of the type *cis*-$[M(CO)_4(PX_2)_2NR]$ [4a]. This clearly indicates the strong π-acceptor ability of cyclodiphosphazane ligands (**1**,**2**).

The ^1H and ^{31}P NMR data for complexes **3**–**6** are listed in Table 2. The ^{31}P NMR spectra of these complexes show two resonances owing to the presence of two different phosphorus nuclei. The resonances of the uncoordinated phosphorus appear in the range 127–130 ppm. For molybdenum and tungsten complexes (**4**–**6**), $^2J(PP)$ is too small to be observed, whereas for the chromium complex **3** an [AX] pattern centred at 181.8 and 128.4 ppm with a $^2J(PP)$ of 10 Hz, is observed.

Reactions with rhodium derivatives

The reaction of $[^tBuNP(OPh)]_2$ with two molar equivalents of $[RhCl(COD)]_2$ in benzene at room temperature gives the mononuclear complex, $[RhCl(COD)(^tBuNP(OPh))_2]$ (**7**) (yield 68%). This complex is moderately stable to air in solution and in the solid state. There is a precedent for this type of complex in the work of Nixon and coworkers [2b], who reported the rhodium complexes, $[RhCl(COD)(^tBuNPX)_2]$ (X = F or Cl).

The reaction of $[^tBuNP(OPh)]_2$ with $[RhCl(CO)_2]_2$ in (2:1 molar ratio) in benzene affords the dinuclear complex, $[RhCl(CO)(^tBuNP(OPh))_2]_2$ (**8**) as indicated by elemental analysis and molecular weight measurements in benzene [17]. A similar complex of $(^tBuNPCl)_2$ was reported by Jenkins and Willey, though no spectroscopic data were presented in support of the structure assigned [1e]. However, this type of coordination of cyclodiphosphazanes is observed in the rhenium complex, $[Re_2(\mu\text{-}Br)_2(CO)_6\{\mu\text{-}(^tBuNPMe)_2\}]$ reported by Scherer et al. [3b].

The IR spectrum of complex **8** shows a strong $\nu(CO)$ frequency at 2020 cm^{-1} characteristic of CO groups *trans* to Cl. The ^{31}P NMR spectrum of complex **8** shows a doublet centred at 120.0 ppm with a $^1J(RhP)$ of 158.6 Hz. In contrast, the ^{31}P NMR spectrum of complex **7** shows two sets of resonances, only one of which exhibits a large doublet splitting due to the coupling of ^{31}P to the ^{103}Rh nucleus

[$^1J(RhP) = 231$ Hz]. This feature clearly indicates the η^1-bonding mode of the cyclodiphosphazane ligand.

Reactions with palladium and platinum derivatives

The reactions of two equivalents of [^{t}BuNP(OPh)]$_2$ with [MCl$_2$(COD)] (M = Pd, Pt) in CH_2Cl_2 at the reflux temperature give monomeric complexes of the type [MCl$_2${(^{t}BuNP(OPh))$_2$}$_2$] in which cyclodiphosphazanes exhibit monodentate mode of coordination. In the case of palladium, a mixture of *cis*- and *trans*-isomers is obtained in a 1:1 ratio whereas the reaction with [PtCl$_2$(COD)] gives exclusively the *cis*-isomer. The reaction of [^{t}BuNP(OPh)]$_2$ with *trans*-[PdCl$_2$(PhCN)$_2$] in 2:1 molar ratio gives pure *trans*-isomer in 80% yield. These complexes are similar to those of (^{t}BuNPX)$_2$ (X = Cl, F) reported by Nixon and coworkers [2a]. The structure of the fluoro-cyclodiphosphazane complex, has been confirmed by single crystal X-ray diffraction [19].

The IR spectrum of the platinum complex **10** shows ν(Pt–Cl) bands at 284 and 302 cm^{-1} attributed to Cl atoms trans to phosphorus atoms. The IR spectrum of a *cis*- and *trans*-mixture of the palladium complex show ν(Pd–Cl) bands at 298 and 315 cm^{-1} and 347 and 355 cm^{-1}, respectively, for *cis*- and *trans*-isomers. The IR spectrum of pure *trans*-isomer shows ν(Pd–Cl) bands at 347 and 355 cm^{-1}.

The ^{1}H NMR spectrum of the product obtained from the reaction of (^{t}BuNP(OPh))$_2$ with [PdCl$_2$(COD)] shows two distinct resonances for *N*-tert-butyl protons, at 1.55 ppm and 1.50 ppm, indicating the presence of two isomers, whereas the *trans*-isomer obtained from the reaction of (^{t}BuNP(OPh))$_2$ with *trans*-[PdCl$_2$(NCPh)$_2$] shows only one resonance at 1.50 ppm. The ^{1}H NMR spectrum of the platinum complex shows a single resonance for *N*-tert-butyl protons, at 1.51 ppm. The structures assigned to these complexes are supported by ^{31}P NMR spectroscopic data.

The ^{31}P NMR spectrum of the platinum complex **10** shows a clear AX pattern. The ^{31}P resonance due to coordinated phosphorus is centred at 44.4 ppm with platinum satellites [$^1J(PtP) = 4836$ Hz], and the signal is split further by coupling to the uncoordinated phosphorus nucleus [$\delta(P_X) = 125.8$ ppm; $^2J(P_AP_X) = 7.6$ Hz]. The uncoordinated phosphorus nucleus also exhibits ^{195}Pt satellites from which $^3J(PtP_X)$ can be calculated to be 22.7 Hz. The large $^1J(PtP_A)$ coupling is attributed to *cis*-configuration. The ^{31}P NMR spectra of palladium complexes **9a** and **9b** show two sets of triplets (see Table 2). The low field resonances are attributed to the uncoordinated phosphorus nucleus. The two well-resolved sets of triplets for each isomer can be interpreted in terms of a deceptively simple [AX]$_2$ spin system in which $^2J(AA') \gg {}^2J(AX)$ [20].

Conclusions

The reactions of [^{t}BuNP(OPh)]$_2$ with transition metal organometallic derivatives have led to the isolation of several interesting complexes such as *cis*-[M(CO)$_4$L$_2$] (L = η^1-[^{t}BuNP(OPh)]$_2$), which are the first examples of group 6 metal tetracarbonyl derivatives containing two monodentate cyclodiphosphazane ligands. The present work, as well as earlier studies, clearly demonstrate the tendency of these ligands to prefer either monodentate or bridged bidentate modes of coordination. There is no firm evidence for the formation of chelate complexes of cyclodiphosphazanes [21]. The complexes isolated in the present study containing one or more η^1-coordinated $[^tBuNP(OPh)]_2$ ligands can serve as valuable synthons for preparing a variety of homo- and hetero-bimetallic complexes and high nuclearity clusters.

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13 $(^tBuNP(OC_6H_4Br\text{-}p))_2$ (2) Yield 68% M p 89–90°C ^1H NMR ($CDCl_3$) 1 35 (s, ^tBu), 7 22 (m, $OC_6H_4Br\text{-}p$) ^{31}P NMR ($CHCl_3$) δ 141 0 (s) Anal Found C, 43 7; H, 4 7; N, 5 1. $C_{20}H_{26}N_2P_2O_2Br_2$ calcd C, 43 7, H, 4 7, N, 5 1% The product formed initially shows the presence of both *trans* and *cis* isomers in 1 2 ratio, with δ (P) values of 234 and 141 ppm respectively [14,15] The *cis*-isomer is obtained in a pure state by fractional crystallization from a 1/3 mixture of CH_2Cl_2 and light petroleum

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