Synthesis of α,ω-Bis(diphenylphosphino)alkane and α,ω-Bis(diphenylphosphino)-(poly)ether Ligands and Complexes of Rhodium(I)

D. HARRY M. W. THEWISSEN, KLAAS TIMMER, JAN G. NOLTES, JAN W. MARSMAN

Institute of Applied Chemistry T.N.O., P. O. Box 5009, 3502 JA Utrecht, The Netherlands

and RICHARD M. LAINE

S.R.I. International, Physical Organic Chemistry Department, 333 Ravenswood Ave, Menlo Park, Calif. 94025, U.S.A.

Received April 16, 1984

Abstract

α,ω-Bis(diphenylphosphino)alkane and α,ω-Bis-(diphenylphosphino)(poly)ether ligands can be prepared in very high yields *via* reaction of the appropriate dihalide with two equivalents of $LiPPh_2$. For the $[Rh(COD)(\overset{\frown}{P\ P})][ClO_4]$ complexes of these ligands, the $\overset{\frown}{P\ P}$ ligands with five or less atoms in the alkane or ether bridge form monomeric complexes via η^2-coordination. In general the ligands with eight or more atoms in the bridge give di- or polynuclear species. In addition the long chain diphosphino-polyethers form – to a small extent – monomeric species by η^2-coordination.

Introduction

Rhodium phosphine complexes are widely used in catalysis and are applied in such important industrial processes as hydroformylation [1]. In hydroformylation type reactions, the key step is the migration of an alkyl group to coordinated carbon monoxide to yield an acyl species. Acyl formation can be promoted in the presence of a cation [2, 3]. In fact, cation binding by the product molecule can be utilised to activate coordinated carbon monoxide towards nucleophilic addition [2, 3]. These cations can be 'stored' in macrocyclic compounds of crown ether type. By incorporation of ether functions, suitable phosphines can be designed which upon coordination to a transition metal form defined crown ether cavities.

In the literature, two possibilities to create a cycle in the neighbourhood of the metal have been described. The most elegant approach is the use of phosphorus(III)-containing macrocycles as ligands. Recently, the first crown ether type phosphorus-(III)-containing macrocycles have been reported by Kyba *et al.* [4]. Lately, the synthesis and complexing properties of monophospha-crown ethers have also been described [5]. In the second approach, a cycle is realized via chelation of a diphosphino-(poly) ether ligand. The first example of complexes of such ligands are *cis*-$Ni(Ph_2P(CH_2CH_2O)CH_2CH_2PPh_2)Cl_2$ [6] and *cis*-$Ni(Ph_2P(CH_2CH_2O)_2CH_2CH_2PPh_2)I_2$ [7]. Alcock and co-workers have reported the structures of the rhodium carbon monoxide complexes *trans*-$[Rh(CO)(Ph_2P(CH_2CH_2O)CH_2CH_2PPh_2)][PF_6]$, *trans*-$[Rh(CO)(H_2O)(Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2)][PF_6]$ [8], and *trans*-$[Rh(CO)(ethanol)(Ph_2P(CH_2CH_2O)_2CH_2CH_2PPh_2)][PF_6]$ [9]. Interestingly, in the last two cases the fourth coordination site is occupied by a water and an ethanol molecule, respectively. These solvent molecules are encapsulated within the macrocyclic ring and are hydrogen bonded to ring oxygen atoms. Recently, Hill *et al.* have shown that $Ni(Ph_2P(CH_2CH_2O)_2CH_2CH_2PPh_2)X_2$ complexes can also include solvent molecules. Depending on the solvent used, the diphosphino-(poly)ether can act either as a quadridentate or as a bidentate ligand [10]. Powell recently described the first example of a cation, stored in the cavity of a crown ether type chelating phosphinite complex, namely $Mo(CO)_3(PhOLi)(Ph_2P(OCH_2CH_2)_3OPPh_2)$ [2]. In this compound the acyl species is indeed stabilized by strong Li^+ cation binding.

To date, there is little information available concerning the application of phosphino(poly)ether complexes as catalysts, despite the novel potential already visible in Powell's work. In the process of pursuing the use of diphosphino(poly)ether ligand rhodium complexes as catalysts we have invested considerable effort in the synthesis of prototype ligands and complexes of these ligands. We report here the synthesis of diphosphino(poly)ether ligands and their complexes with rhodium(I). For reasons of comparison we have also prepared the analogous $Rh(Ph_2P(CH_2)_nPPh_2)$ complexes (n = 2, 5, 8, 11), a few of which have been previously described in the literature. The different coordination modes of the ligands (*cis, trans,* bridged) are discussed.

0020-1693/85/$3.30

TABLE I. Analytical Data of Rh-Complexes, Calculated Values in Parentheses.

Complex	C	H	P[a]	Cl	O
$[Rh(COD)(PPh_3)_2][ClO_4]$	62.79	5.08	7.14	4.26	7.41
	(63.29)	(5.03)	(7.43)	(4.24)	(7.67)
$[Rh(COD)(Ph_2P\frown PPh_2)][ClO_4]$	57.04	5.19	7.53	4.83	
	(57.60)	(5.08)	(8.75)	(5.00)	
$[Rh(COD)(Ph_2P\frown\frown PPh_2)][ClO_4]$	55.37	5.56	6.95	4.72	
	(59.18)	(5.60)	(8.26)	(4.72)	
$[Rh(COD)(Ph_2P\frown\frown\frown PPh_2)][ClO_4]$	56.05	5.96	6.47	4.44	
	(60.58)	(6.06)	(7.83)	(4.47)	
$[Rh(COD)(Ph_2P\frown\frown\frown\frown PPh_2)][ClO_4]$	58.37	6.39	5.93	4.15	
	(61.85)	(6.47)	(7.43)	(4.24)	
$[Rh(COD)(Ph_2P\frown O\frown PPh_2)][ClO_4]\cdot 0.2\,CH_2Cl_2$	56.63	5.16	7.34	5.29	10.38
	(56.94)	(5.28)	(8.15)	(5.28)	(10.52)
$[Rh(COD)(Ph_2P\frown O\frown O\frown PPh_2)][ClO_4]$	51.42	5.27	6.87	4.68	
	(57.27)	(5.53)	(7.79)	(4.45)	
$[Rh(COD)(Ph_2P\frown O\frown O\frown O\frown PPh_2)][ClO_4]$	52.67	5.62	6.52	4.29	
	(57.12)	(5.71)	(7.38)	(4.21)	

[a]Our P analysis in compounds containing heavy metals is difficult to perform. Systematically too low P percentages are found.

Experimental

Reactions were carried out under nitrogen at room temperature, unless otherwise noted, in analytical grade solvents. Ph_2PCl and Ph_2PH (Ventron), PPh_3 and $Ph_2P(CH_2)_2PPh_2$ (Fluka), $Br(CH_2)_5Br$ (Merck), $Br(CH_2)_8Br$ (Ega-Aldrich), $Br(CH_2)_{11}Br$, $Cl(CH_2CH_2O)CH_2CH_2Cl$ and $Cl(CH_2CH_2O)_2CH_2$-CH_2Cl (Fluka), $RhCl_3\cdot 3H_2O$ (Strem), AgOTf (Aldrich), nBu-Li/hexane (Merck) and tetraethyleneglycol (Fluka) were commercially obtained. $[Rh(COD)Cl]_2$ [11] and Rh(COD)(acac) [12] were synthesised according to literature procedures.

Microanalyses were performed at the element-analytical department of the Institute of Applied Chemistry TNO, Zeist and by Prof. Dipl. Ing. H. Malissa and G. Reuter, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, F.R.G. Routine infrared spectra were measured on a Perkin-Elmer 577 spectrophotometer (4000–200 cm^{-1}) in CsI discs. Infrared frequencies are in units of reciprocal centimeters (s = strong, m = medium, w = weak, sh = shoulder, br = broad). NMR spectra were recorded on a Bruker WH 90 spectrometer. ^1H NMR chemical shifts are given in units of δ, relative to TMS (s = singlet, d = doublet, t = triplet, q = quartet, qi = quintet, st = sextet, m = multiplet). ^{13}C NMR shifts were recorded at 22.63 MHz relative to TMS. ^{31}P NMR shifts were measured at 36.44 MHz relative to an external 85% H_3PO_4 standard. Couplings are given in Hz.

Analytical data for the rhodium complexes are given in Table I.

Preparation of $Br(CH_2CH_2O)_3CH_2CH_2Br$

17.08 g of bromine was added dropwise (temp. <55 °C) to a solution of 28 g of PPh_3 and 9.7 g of tetraethyleneglycol in 100 ml of DMF until no discolouration of the bromine took place. Stirring was continued for 1 hr. After filtration and evaporation of the solvent, 200 ml of diethylether and 100 ml of water were added to the residue. The two layers were filtered and the solid ($OPPh_3$) was washed with diethyl ether. After separation, the organic layer was washed with water to remove DMF, and dried on Na_2SO_4. After filtration and concentration to 50 ml, the remainder of the $OPPh_3$ crystallised at −20 °C. After filtration and evaporation of the solvent, the residue was fractionally distilled at 0.05–0.1 mm Hg. Yield: 11.0 g (68.8%) of fraction with b.p. 120–122 °C. *Anal.* Calcd.: C 30,16, H 4.99, O 15.03, Br 49.96; found: C 30.02, H 5.00, O 15.01, Br 49.97. ^1H NMR ($CDCl_3$) δ($BrCH_2$–CH_2O) 3.34–3.98 (8H), δ(OCH_2CH_2O) 3.69 (8H). ^{13}C NMR $Br\overset{1}{\frown}\overset{2}{\frown}O\overset{3}{\frown}\overset{4}{\frown}O$ δ (C_1) = 30.38, δ (C_2) = 71.20, δ (C_3) = 70.55, δ (C_4) = 70.66.

Preparation of [Rh(COD)OTf]

2.5 g of $[Rh(COD)Cl]_2$ were added to a solution of 2.57 g of AgOTf in 50 ml of acetone. The orange solution was stirred for 15 min. After filtration of AgCl and washing with acetone, the solvent was evaporated , 25 ml of diethylether was added and the solution was dried on $MgSO_4$ for one hour. After filtration and evaporation of the solvent, the residue was dried. Yield: 80–90%, Melting traject 115–190 °C (decomposition). *Anal.* calcd.: C 30.25, H 3.62; F 15.55, Cl 0.0; found: C 30.00, H 3.33, F 15.83, Cl 0.0. ^1H NMR ($CDCl_3$) δ(alkene) = 4.2 (4H), δ(aliph) = 1.6 and 2.5 (8H). IR (CsI disc) ν(C=C) = 1645 cm^{-1} (m–s). Mol. weight, determined osmometrically in acetone: 355. Calcd: 360.

Preparation of $Ph_2P(CH_2)_nPPh_2$ (n = 5, 8, 11) and $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ (n = 1, 2, 3)

a) A bis-Grignard reagent was prepared by reaction of 25 mmol of the appropriate dihalogenide and 55 mAt Mg (slight excess) in 25 ml of THF. Based on 90% yield, a solution of 45 mmol of Ph_2PCl in 10 ml of THF was added dropwise in 1 h under vigorous stirring. Stirring was continued for 2 h, 25 ml of oxygen-free water was added. After removal of the water layer, the organic layer was washed with 25 ml of water.

The ether layer was dried on $MgSO_4$. After filtration and evaporation of the solvent, the products crystallised or were distilled at low pressure (10^{-3}–10^{-4} mm Hg). Yields 50–60%.

b) A reaction mixture, containing 50 mmol of PPh_3, 107 mAt of freshly cut Li (slight excess) and 85 ml of THF, was stirred vigorously for 6 h at 45–50 °C, and for 16 h at room temperature. The colour changed gradually to dark red. A solution of 4.63 g of freshly distilled tBuCl in 15 ml of THF was added dropwise to remove the formed PhLi. Evolution of isobutene was observed and the colour turned to light red. Upon cooling to 0 °C, a solution of 25 mmol of the appropriate dihalogenide in 50 ml of THF was added dropwise in 45 min and the mixture was stirred for 4 h at room temperature. The work-up was similar to the procedure described for method a). Yields 70–75%.

c) The easiest and preferable method. 20 mmol of nBuLi in hexane was added dropwise in 0.5 h at 0 °C to a solution of 20 mmol of PPh_2H in 25 ml of diethylether. The yellow suspension was then refluxed for 1 h. Upon cooling to room temperature a solution of 10 mmol of the appropriate dihalogenide in 5 ml of diethylether was added dropwise in 45 min. Again the mixture was refluxed for 1 h. In the case of chloride, the solid LiCl was filtered off. The work-up was similar to the procedure described for method a). Yields: 90–97%.

Preparation of $[Rh(COD)(PPh_3)_2][ClO_4]$

765 mg of PPh_3 was added in portions to a mixture of 360 mg of $[Rh(COD)Cl]_2$ and 250 mg of $NaClO_4 \cdot H_2O$ in 25 ml of acetone. Upon addition of half the amount of PPh_3 the solution was bright, whereas upon addition of 90% an orange precipitate formed. Extra acetone was added and the red mixture was stirred for 5 min. After evaporation of the solvent, and addition of 10 ml of CH_2Cl_2 to the residue, the solid NaCl and $NaClO_4$ were filtered. The filtrate was concentrated to 5 ml, 5 ml of ethanol was added and upon slow addition of 75 ml of diethyl ether, orange crystals formed. Yield: 78%.

Preparation of $[Rh(COD)(\widehat{P\ P})][ClO_4]$, $\widehat{P\ P}$ = $Ph_2P(CH_2)_nPPh_2$ (n = 2, 5, 8, 11) and $\widehat{P\ P}$ = $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ (n = 1, 2, 3)

A solution of 1.99 mmol of 70% $HClO_4$ in 2.5 ml THF was added to a solution of 2.00 mmol of Rh(COD)acac in 7.5 ml of THF. The colour changed from yellow to light orange. Then 1.94 mmol of the appropriate diphosphine in THF, the amount of which depends on the phosphine used (for longer chain phosphines higher dilutions are required) was added, the colour of the solution becoming reddish. Stirring was continued for 0.5 h. The products were isolated by slow addition of diethyl ether (sometimes preceded by partial evaporation of THF). All compounds were recrystallised by dissolution in minimal CH_2Cl_2 and addition of equal volume of ethanol. All compounds required stepwise addition of diethyl ether to complete crystallisation. Yields: 90–95%.

Results and Discussion

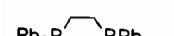
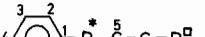
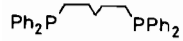
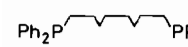
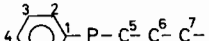
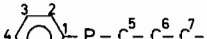
Diphosphine Ligands

The preparation of the ligands used in this paper has been reported previously by several authors, *viz.* $Ph_2P(CH_2)_5PPh_2$ in ref. [14], $Ph_2P(CH_2)_8PPh_2$ and $Ph_2P(CH_2)_{11}PPh_2$ in ref. [15], $Ph_2P(CH_2CH_2O)CH_2CH_2PPh_2$ in ref. [16], $Ph_2P(CH_2CH_2O)_2CH_2CH_2PPh_2$ in ref. [17] and $Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2$ in ref. [18]. Various synthetic methods have been applied. So far as the $tBu_2P(CH_2)_nPt\text{-}Bu_2$ derivatives are concerned, the most convenient procedure was described by Shaw *et al.* [14]. These diphosphine ligands were prepared via reaction of two equivalents of t-Bu_2PH with one equivalent of the appropriate dibromide, which gives the diphosphonium species. Unfortunately, this method cannot be used in the case of aryl-substituted phosphines, since facile cyclization is known to occur [19].

As described in the experimental section, we utilized 3 synthetic routes to prepare the various ligands. Method 'a' proceeds via the reaction of a bis-Grignard reagent with two equivalents of diphenylphosphine chloride. Procedures 'b' and 'c' involve the reaction of a dihalide with two equivalents of lithium diphenylphosphide prepared *in situ*. In method 'b' the $LiPPh_2$ is formed from triphenylphosphine. This procedure is essentially identical with that developed by Aguiar *et al.* [13]. In method 'c' diphenylphosphine serves as the starting material. No side products are obtained with method 'c', thus making it the synthetic method of choice. Moreover, the highest yields are obtained with this method, *viz.* in the order of 90–97%.

The NMR data for the various ligands are given in Table II. These are in accordance with the literature values, as far as published. The diphosphines are

TABLE II. NMR Data of the Diphosphine Ligands.

Ligand	^{1}H NMR	^{31}P{^{1}H}NMR	^{13}C{^{1}H}NMR
	measured in C_6D_6	Measured in $CDCl_3$	measured in $CDCl_3$
	δ(aliph) = 2.09t J(P) = 8.2 (4H) δ(arom) = 7.3 (20H) measured in $CDCl_3$	δP = −12.40	 δ(C_1) = 138.08t J(P*) = 13.6 δ(C_2) = 132.64t J(P*) = 18.8 δ(C_3) = 128.36t J(P) = 6.7 δ(C_4) = 128.54s J(P) = 0 δ(C_5) = 23.80d J(P) = 1.9 J(P–P) = 33.8 J(P□) = 0
mp. 143–145 °C			
	δ(aliph) = 1.02–2.13 (10H) δ(arom) = 7.05–7.15 (20H)	δP = −16.11 measured in C_6D_6	 δ(C_1) = 138.80 J(P) = 13.23 δ(C_2) = 132.58 J(P) = 18.38 δ(C_3) = 128.24 J(P) = 6.61 δ(C_4) = 128.33 J(P) = 0 δ(C_5) = 27.67 J(P*) = 11.39 δ(C_6) = 25.37 J(P*) = 16.17 δ(C_7) = 32.44t J(P*) = 12 J(P□) = 0
mp. 46–49 °C bp. 180–200 °C/10^{-3} mm Hg			
	δ(aliph) = 0.83–2.12 (16H) δ(arom) = 7.04–7.15 7.37–7.50 (20H)	δP = −16.03	 δ(C_1) = 138.94 J(P) = 12.86 δ(C_2) = 132.58 J(P) = 18.01 δ(C_3) = 128.24 J(P) = 6.61 δ(C_4) = 128.30 J(P) = 0 δ(C_5) = 27.88 J(P) = 11.39 δ(C_6) = 25.76 J(P) = 16.17 δ(C_7) = 30.97 J(P) = 12.86 δ(C_8) = 28.90 J(P) = 0
mp. 101–102 °C			
	δ(a) = 2.025t (4H) δ(aliph) = 1.2–1.5 (18H) δ(arom) = 7.2–7.5 (20H) measured in $CDCl_3$	δP = −16.02	 δ(C_1) = 138.94 J(P) = 13.23 δ(C_2) = 132.58 J(P) = 18.38 δ(C_3) = 128.22 J(P) = 6.61 δ(C_4) = 128.29 J(P) = 0
mp. 42–43 °C			

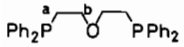
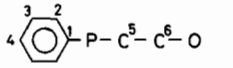
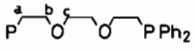
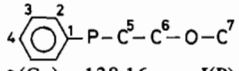
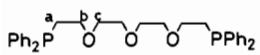
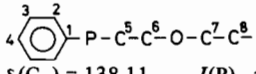
	δ(a) = 2.27qi (4H) δ(b) = 3.37t (4H)	δP = −22.05	 δ(C$_1$) = 138.15 J(P) = 12.50 δ(C$_2$) = 132.58 J(P) = 18.75 δ(C$_3$) = 128.31 J(P) = 6.98 δ(C$_4$) = 128.48 J(P) = 0 δ(C$_5$) = 28.65 J(P) = 12.86 δ(C$_6$) = 67.80 J(P) = 24.63
oil	δ(arom) = 6.87–7.6 (20H)		δ(C$_5$) = 27.91 J(P) = 11.03 δ(C$_6$) = 25.81 J(P) = 16.17 δ(C$_7$) = 31.05 J(P) = 12.86 δ(C$_8$) = 29.20 J(P) = 4.78 δ(C$_9$) = 29.31 J(P) = 0
	δ(a) = 2.34st (4H) J(P–H) = 7.81 δ(b) = 3.23t (4H) δ(c) = 3.28t (4H)	δ(P) = −22.17	 δ(C$_1$) = 138.16 J(P) = 12.50 δ(C$_2$) = 132.58 J(P) = 18.75 δ(C$_3$) = 128.33 J(P) = 6.98 δ(C$_4$) = 128.48 J(P) = 0 δ(C$_5$) = 28.61 J(P) = 12.50 δ(C$_6$) = 68.46 J(P) = 25.73 δ(C$_7$) = 69.92 J(P) = 0
mp. 54–55 °C	δ(arom) = 7.00–7.14 7.32–7.51 (20H)		
	δ(a) = 2.35st J(P–H) = 7.87 (4H) δ(b) = 3.55t (4H) δ(c) = 3.38m (8H)	δ(P) = −21.82	 δ(C$_1$) = 138.11 J(P) = 12.13 δ(C$_2$) = 132.58 J(P) = 18.75 δ(C$_3$) = 128.34 J(P) = 6.98 δ(C$_4$) = 128.48 J(P) = 0 δ(C$_5$) = 28.57 J(P) = 12.50 δ(C$_6$) = 68.40 J(P) = 25.00 δ(C$_7$) = 69.99 J(P) = 0 δ(C$_8$) = 70.44 J(P) = 0
oil	δ(arom) = 7.01–7.15 7.28–7.51 (20H)		

TABLE III. $^{31}P\{^1H\}$ NMR Data of the [Rh(COD)($Ph_2\widehat{P}\ \widehat{P}Ph_2$)][$ClO_4$] Complexes. Measured in $CDCl_3$.

Compound		δP	^1J(Rh–P)	$^2J(P-P)_{cis}$
[Rh(COD)(PPh_3)$_2$][ClO_4][a]		26.22	145.26	
[Rh(COD)($Ph_2P\frown PPh_2$)][ClO_4][b]		56.27	149.53	
[Rh(COD)($Ph_2P\frown\frown PPh_2$)][ClO_4][c]	*a*[d]	7.33	141.60	
	b	(24.83)	(146.42)	
[Rh(COD)($Ph_2P\frown\frown\frown PPh_2$)][$ClO_4$]	*a*	18.02	142.21	
	b	19.94 (P1, P2)	142.51	26.51
	c	23.53	148.62	
[Rh(COD)($Ph_2P\frown\frown\frown\frown PPh_2$)][$ClO_4$]	*a*	20.58	142.51	
	b	18.47 (P1, P2)	142.51	23.49
	c	24.11	148.31	
[Rh(COD)($Ph_2P\frown O\frown PPh_2$)][$ClO_4$]		11.91	144.32	
[Rh(COD)($Ph_2P\frown O\frown O\frown PPh_2$)][$ClO_4$]	*a*	12.27	144.34	
	c	21.05	153.50	
	d	35.08 (P1)	119.62	22.88
		47.32 (P2)	131.22	22.88
	e	45.44	125.44	
	f	35.75		
[Rh(COD)($Ph_2P\frown O\frown O\frown O\frown PPh_2$)][$ClO_4$]	*a*	12.67	144.65	
	b	21.05	127.86	
	c	23.35	151.36	
	e	41.45	130.00	
	f	35.57		
	g	56.20	148.00	

[a] ^1H NMR in $CDCl_3$; δ(alkene) 4.62 (4H); δ(aliph) 1.1–1.4 (8H); δ(arom) 7.2–7.5 (29H). [b] ^1H NMR in $CDCl_3$: δ(alkene) 4.94 (4H); δ(aliph) 1.64 and 2.1–2.4 (15H); δ(arom) 7.5–7.6 (22H). [c] ^1H NMR in $CDCl_3$: δ(alkene) 4.63 (3H); δ(aliph) 1.7 (21H), δ(arom) 7.3–7.9 (20H). [d] Symbols *a* through *g* relate to the various isomers (see text).

solids or, with increasing chain length, oils, which tend to solidify on repeated purification and recrystallization. In solution they are slightly oxygen sensitive.

[Rh(COD)($\widehat{P}\ \widehat{P}$)][ClO_4] Complexes; $\widehat{P}\ \widehat{P}$ = $Ph_2P(CH_2)_nPPh_2$ (n = 2, 5, 8, 11) and $\widehat{P}\ \widehat{P}$ = $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ (n = 1, 2, 3)

In some instances, the same or analogous compounds, especially with the short chain ligands, have been reported in the literature [20, 22–24], but they have not as a group been characterized by ^{31}P NMR spectroscopy. Additionally, rhodium complexes for the longer chain diphosphine ligands have not been described. Schrock and Osborn have undertaken a survey of preparation methods for these types of complexes [20].

We find that the easiest synthetic route to the desired compounds is via reaction between Rh(COD)-acac, $HClO_4$, and the appropriate diphosphine. The yields are very high, varying from 90–95%. Because the [Rh(COD($\widehat{P}\ \widehat{P}$)][ClO_4] complexes react rapidly with a second diphosphine, through COD displacement, slightly less than one equivalent of the diphosphine has been used. The complexes are fairly stable towards oxygen and moisture, but they tend to lose COD on standing; COD loss is then followed by oxidation. The carbon analyses reflect this phenomenon. The presence of solvents such as CH_2Cl_2, shown by the ^1H NMR spectra, also accounts for the low C percentages.

The NMR parameters of the complexes are given in Table III. For comparison we have also prepared the known bis triphenylphosphine complex [Rh(COD)(PPh_3)$_2$][ClO_4], whose ^{31}P NMR has not been published [20, 21]. The values of δ = 26.22 ppm and ^1J(Rh–P) = 145.26 Hz are in agreement with the values of 27.5 ppm and 156 Hz, respectively, found for [Rh(bicyclo[2.2.1]heptadiene)(PPh_3)$_2$][BF_4] [22].

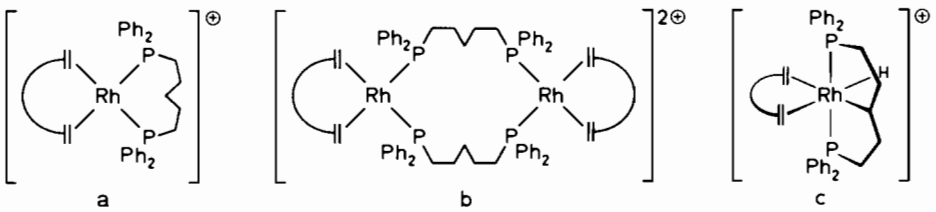


Fig. 1. Possible structures of $[Rh(COD)(Ph_2P(CH_2)_5PPh_2)][ClO_4]$: a, Monomer; b, Dimer; c, Cyclometallation (see text).

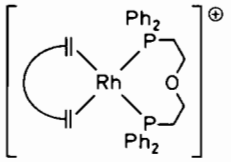


Fig. 2. Structure of $[Rh(COD)(Ph_2P(CH_2CH_2O)CH_2CH_2PPh_2)][ClO_4]$.

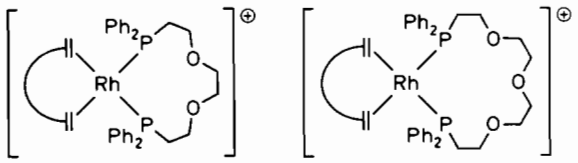


Fig. 3. Monomeric structure of $[Rh(COD)(Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2)][ClO_4]$ (n = 2, 3).

For the known complex $[Rh(COD)(Ph_2P(CH_2)_2PPh_2)][ClO_4]$ we find δ = 56.27 ppm and ^1J(Rh–P) = 149.53 Hz, whose ^1J(Rh–P) coupling is comparable to that of the bis-PPh_3 complex. The literature reports values of 54.6 ppm and 161 Hz [20] and of 58.3 ppm and 132.1 Hz [23], respectively, for the mono diphos complex. The latter data are most probably incorrect, as they compare quite well with our data for the complex $[Rh(Ph_2P(CH_2)_2PPh_2)_2][OTf]$, *viz.* 58.46 ppm and 132.45 Hz, respectively.

The ^{1}H NMR spectrum of $[Rh(COD)(Ph_2P(CH_2)_5PPh_2)][ClO_4]$ has been reported but the compound was not characterized by ^{31}P NMR [24] which shows one doublet signal with δ = 7.33 ppm and ^1J(Rh–P) = 141.60 Hz. We assign this signal to a species having a monomeric structure with two phosphine groups in *cis*-position (structure *a* in Fig. 1). Unpurified samples of this compound show a second doublet at 24.83 ppm with ^1J(Rh–P) = 146.42 Hz. We think that this signal arises from a diphosphine bridged complex *b*, a possible structure of which is given below. Another possibility, though less probable, is cyclometallation, giving a Rh(III) complex, *viz.* $[Rh(COD)H(Ph_2(CH_2CH_2)CH(CH_2CH_2)PPh_2]^+$, in analogy to those reported by Shaw *et al.* [13, 25–26].

The spectra of $[Rh(COD)(Ph_2P(CH_2)_nPPh_2)][ClO_4]$ (n = 8, 11) indicate the presence of three species, the structures of which are not clear. In view of the high δ values we assume that these complexes possess diphosphine bridges rather than *cis*-coordinated diphosphine. Again, cyclometallation may have taken place. Because of the long aliphatic chains, the formation of *trans* complexes is also possible [15a, 27]; however the formation of *trans*-Rh(I)-(COD)(P⌒P) complexes can be excluded because of the presence of COD which must coordinate *cis*. However, upon cyclometallation a *trans* configuration is possible.

For the rhodium diphosphino(poly)ether complexes, we observed a similar trend. The ^{31}P NMR spectrum of $[Rh(COD)(Ph_2P(CH_2CH_2O)CH_2CH_2PPh_2)][ClO_4]$ shows one doublet at 11.91 ppm with ^1J(Rh–P) = 144.32 Hz. The structure of this complex is given in Fig. 2.

For the longer chain ligand complexes, *i.e.* $[Rh(COD)(Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2)][ClO_4]$ (with n = 2, 3), several species are again found. In contrast to the aliphatic chain diphosphines, $Ph_2P(CH_2)_nPPh_2$ (n = 8, 11), the ether containing ligands form both monomeric species *a*, with δ = 12.27 ppm, ^1J(Rh–P) = 144.34 Hz, and δ = 12.67 ppm, ^1J(Rh–P) = 144.65 Hz, respectively, and dimeric or polymeric products with considerably higher δ values. The formation of the monomeric species may be promoted by interactions of the ether oxygens with the metal centre (chelation effect). The species *f* (singlets at δ = 35.75 ppm and at δ = 35.57 ppm, respectively) are most probably decomposition products, since these δ values more or less coincide with the δ values of the analogous phosphine oxides (see also Table IV). The nature of the other species is uncertain. Most probably dimerization or polymerization has taken place. The ether oxygens may also be involved in the coordination. The presence of *trans* diphosphine chelates is also possible.

Summarizing, we can state that for the $[Rh(COD)(P⌒P)][ClO_4]$ complexes the P⌒P ligands with five or less atoms in the bridge form mononuclear complexes, in which the diphosphine is η^2-coordinated. The longer chain ligands, with eight or more atoms in the bridge form in principle di- or polynuclear species. In contrast with the diphosphinoalkanes, the diphosphino(poly)ethers also form, though to a lesser degree, monomeric species with η^2-coordination of the ligand. In the case of the diphosphinoalkanes cyclometallation may take place.

Acknowledgements

Support by NATO (Grant R.G. 020.080, to R. M. L. and D. H. M. W. T.) is gratefully acknowledged. R. M. L. also thanks NSF for support of this work through CHE Grant Nos. 78–25069 and 82–19461.

References

1 P. Pino, F. Piacenti and M. Bianchi, *'Organic Syntheses via Metal Carbonyls'*, I. Wender and P. Pine, Eds., Wiley–Intersci., New York, N.Y. 1977, pp. 136–197.
2 a) J. Powell, A. Kuksis, C. F. May, S. C. Nyburg and S. J. Smith, *J. Am. Chem. Soc., 103,* 5941 (1981), and references 1–7 therein.
b) J. Powell, M. Gregg, A. Kuksis and P. Meindl, *J. Am. Chem. Soc., 105,* 1064 (1983).
3 S. J. McLain, *J. Am. Chem. Soc., 105,* 6355 (1983).
4 a) E. P. Kyba, A. M. John, S. B. Brown, C. W. Hudson, M. J. McPhaul, A. Harding, K. Larsen, S. Niedzwiecki and R. E. Davis, *J. Am. Chem. Soc., 102,* 139 (1980).
b) E. P. Kyba, R. E. Davis, C. W. Hudson, A. M. John, S. B. Brown, M. J. McPhaul, L. K. Liu and A. C. Glover, *J. Am. Chem. Soc., 103,* 3868 (1981).
5 A. van Zon, G. J. Torny and J. H. G. Frijns, *Recl. Trav. Chim. Pays-Bas, 102,* 326 (1983).
6 P. T. Greene and L. Sacconi, *J. Chem. Soc. A:,* 866 (1970).
7 L. Sacconi and J. Gelsomini, *Inorg. Chem., 7,* 291 (1968).
8 N. W. Alcock, J. M. Brown and J. C. Jeffery, *J. Chem. Soc., Dalton Trans.,* 583 (1976).
9 N. W. Alcock, J. M. Brown and J. C. Jeffery, *J. Chem. Soc., Dalton Trans.,* 888 (1977).
10 W. E. Hill, J. G. Taylor, C. A. McAuliffe, K. W. Muir and L. Manojlovic Muir, *J. Chem. Soc., Dalton Trans.,* 833 (1982).
11 J. Chatt and L. M. Venanzi, *J. Chem. Soc.,* 4735 (1957).
12 D. Sinou and H. B. Kagan, *J. Organomet. Chem., 114,* 325 (1976).
13 a) A. M. Aguiar, J. Beisler and A. Mills, *J. Org. Chem., 27,* 1001 (1962).
b) V. D. Bianco and S. Doronzo, *Inorg. Synth., 16,* 155 (1976).
14 N. A. Salem, H. D. Empsall, R. Markham, B. L. Shaw and B. Weeks, *J. Chem. Soc., Dalton Trans.,* 1972 (1979).
15 a) W. E. Hill, C. A. McAuliffe, I. E. Niven and R. V. Parish, *Inorg. Chim. Acta, 38,* 273 (1980).
b) W. E. Hill, D. M. A. Minahan, J. G. Taylor and C. A. McAuliffe, *J. Chem. Soc. Perkin II,* 327 (1982).
16 L. Sacconi and J. Gelsomini, *Inorg. Chem., 7,* 291 (1968).
17 W. E. Hill, J. G. Taylor, C. A. McAuliffe, K. W. Muir and L. Manojlovic-Muir, *J. Chem. Soc., Dalton Trans.,* 833 (1982).
18 N. W. Alcock, J. M. Brown and J. C. Jeffery, *J. Chem. Soc., Dalton Trans.,* 583 (1976).
19 K. Issleib, K. Krech and K. Gruber, *Chem. Ber., 96,* 2186 (1963).
20 R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc., 93,* 2397 (1971).
21 L. M. Haines, *Inorg. Chem., 9,* 1517 (1970).
22 J. M. Brown, P. A. Chaloner, A. G. Kent, B. A. Murrer, P. N. Nicholson, D. Parker and P. J. Sidebottom, *J. Organomet. Chem., 216,* 263 (1981).
23 G. E. Maciel, D. J. O'Donnell and R. Greaves, *Adv. Chem. Ser., 196,* 389 (1982).
24 D. Sinou and H. B. Kagan, *J. Organomet. Chem., 114,* 325 (1976).
25 J. C. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.,* 1020 (1976).
26 B. L. Shaw, *Adv. Chem. Ser., 196,* 101 (1982).
27 W. E. Hill, D. M. A. Minahan, J. G. Taylor and C. A. McAuliffe, *J. Am. Chem. Soc., 104,* 6001 (1982).