The Synthesis of some Polyether Bridged Diphosphines and their Reaction with Rh(COD)acac

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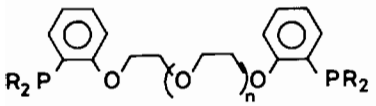
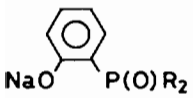
Abstract

The polyether bridged diphosphines,



(n = 1,2) have been prepared in 60–70% yield by reduction of the corresponding diphosphinedioxides with Si_2Cl_6 or $(i\text{-}Bu)_2AlH$. These diphosphinedioxides have been prepared in 75–90% yield by reaction of two equivalents of the appropriate



with one equivalent of di- and triethylene glycol ditosylate.

In general, reaction between the diphosphines, Rh(COD)acac and $HClO_4$ gives a mixture of species, *cis*-[Rh(COD)(P⁀P)][ClO_4] being the main complex. This complex reacts with CO to η^3-*trans*-[Rh(CO)(P⁀O⁀P)][ClO_4].

Introduction

Bidentate neutral organophosphorus compounds with a (poly)ether chain interlinking two phosphorus nuclei are expected to possess special ligating properties and are, as a matter of fact, of potential interest in view of various important applications.

In a previous paper Alberts *et al.* have shown that diphosphinedioxide (poly)ethers can act as a guest for host molecules like amino acid ester salts, in which the host is encapsulated in the cavity of the macrocyclic receptor [1]. Diphosphinedioxides are also likely to have the ability to interact with metal ions. This is of importance with respect to extraction of heavy metals, in particular transplutonium elements. For this purpose bidentate organophosphorus derivatives have proven better extractants than their monodentate analogues, probably due to the chelate effect [2].

Recently, we have also reported on the synthesis of some Rh(COD) diphosphino–(poly)ether complexes [3]. By *cis*-chelation of the diphosphino ligand a macrocycle containing ether functions may be realised in the vicinity of the metal centre. The possibility of storing small less reactive molecules in the polyether cavities of these complexes makes them highly interesting in view of chemical and catalytic reactions.

In this paper we describe the synthesis and spectroscopic characterisation of three α, ω-diphosphinedioxide (poly)ether molecules and the corresponding diphosphino analogues, as well as the interaction of the latter derivatives with Rh(I).

Experimental

Unless noted otherwise, reactions were carried out under nitrogen at room temperature, in analytical grade solvents, which were dried and distilled before use. Si_2Cl_6 (Aldrich), $(i\text{-}Bu)_2AlH$ (Schering A.G.) and 55% NaH in mineral oil (Fluka) were commercially obtained. Diethylene glycol ditosylate (m.p. 87–88 °C) was prepared in 86% yield from diethylene glycol (Fluka) and p-toluene sulfonylchloride (Merck) in pyridine; likewise triethyleneglycol ditosylate (m.p. 75–76 °C) was obtained in 89% yield from triethylene glycol (Fluka). Rh(COD)acac was synthesised according to a literature procedure [4].

Microanalyses were performed at the element-analytical department of the Institute of Applied Chemistry TNO, Zeist. Routine infrared spectra were measured on a Perkin-Elmer 577 spectrophotometer (4000–200 cm^{-1}) in KBr discs. NMR spectra were recorded on a Bruker WH 90 spectrometer in $CDCl_3$ as the solvent. ^{1}H-NMR chemical shifts are given in units of δ, relative to TMS (s = singlet, d = doublet, t = triplet, m = multiplet). ^{13}C-NMR shifts were recorded at 22.63 MHz, relative

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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.

1,5-Di[(2-diphenylphosphineoxido)phenoxy]-3-oxapentane 1

5.88 g (20 mmol) of (*o*-hydroxyphenyl)diphenylphosphineoxide [1] was added to a solution of 0.46 g (20 mmol) of sodium ethoxide in 30 ml of ethanol. After refluxing for one hour and cooling to room temperature 3.73 g (9 mmol) of diethylene glycol ditosylate was added, together with 10 ml of ethanol. The mixture was refluxed for five hours. After evaporation of the solvent 50 ml of CH_2Cl_2 and 50 ml of 0.5 n NaOH in H_2O were added to the residue. Upon shaking, the water layer was removed and the organic layer was washed with 50 ml of 0.5 n NaOH in H_2O and 50 ml of H_2O respectively. The organic layer was dried on $MgSO_4$. After filtration and evaporation of the CH_2Cl_2, the product was recrystallised from CH_2Cl_2/hexane. Initially, the product was obtained as the clathrate with CH_2Cl_2, m.p. 123–124 °C. The solvent molecule is lost upon heating at 130 °C in vacuo for three hours. Yield 90%. *Anal.* Calcd. for formula $C_{40}H_{36}O_5P_2$: C, 72.95, H, 5.47, P, 9.42, O, 12.16, Found: C, 72.44, H, 5.32, P, 9.49, O, 12.43.

1,8-Di[(2-diphenylphosphineoxido)phenoxy]-3,6-dioxaoctane 2

4.26 g (14.5 mmol) of (*o*-hydroxyphenyl)-diphenylphosphineoxide [1] was suspended in 35 ml of DMF. Then 0.7 g of 55% NaH (16 mmol) in mineral oil was added in portions. After vigorous stirring at 80 °C for one hour and cooling to room temperature 2.98 g (6.5 mmol) of triethylene glycol ditosylate was added, together with 10 ml of DMF. Stirring at 80 °C was continued for four hours. The solvent was evaporated and the work-up was similar to the procedure described above. The product was now purified by washing with boiling ether for four hours. Yield: 89%. *Anal.* Calcd. for formula $C_{42}H_{40}O_6P_2$: C, 71.80, H, 5.70, P, 8.83, O, 13.68, Found: C, 71.41, H, 5.54, P, 8.89, O, 13.91.

1,5-Di[(2-methyl phenyl phosphineoxido)phenoxy]-3-oxapentane 3

Methyl (*o*-methoxyphenyl)phenylphosphineoxide was prepared in 94% yield from reaction of *o*-methoxyphenylmagnesium bromide with menthyl methylphenylphosphate (+, –). Subsequent demethylation with BBr_3 gave methyl (*o*-hydroxyphenyl)phenyl phosphineoxide, m.p. 165–167 °C in 74% yield.

9.5 g (41 mmol) of methyl(*o*-hydroxyphenyl)-phenylphosphineoxide was dissolved in 70 ml of DMF. 1.97 g (45 mmol) of 55% NaH in mineral oil was then added in portions. After vigorous stirring at 80 °C for 0.5 h and cooling to room temperature 7.68 g (18.55 mmol) of diethylene glycol ditosylate was added, with 5 ml of DMF. Stirring at 80 °C was continued for five hours. The solvent was removed by evaporation and the work-up was similar to the procedure described for 1. The product was purified by washing with ether at room temperature. Yield 79%. *Anal.* Calcd. for formula $C_{30}H_{32}O_5P_2$: C, 67.41, H, 5.99, P, 11.61, O, 14.98, Found: C, 66.96, H, 6.15, P, 11.32, O, 15.49.

Preparation of the Phosphines (4–6)

Two methods were employed to reduce the phosphineoxides to the corresponding phosphines.

a 15 mmol of the appropriate phosphineoxide was suspended in 40 ml of acetonitrile. 8.07 g (30 mmol) of hexachlorodisilane was added dropwise under vigorous stirring. Stirring was continued for 0.5 h at room temperature, followed by three hours at reflux temperature. Upon cooling to 0 °C, 50 ml of 4 n NaOH in H_2O was added dropwise. After addition of 50 ml of CH_2Cl_2 the remaining precipitate was filtered and washed with CH_2Cl_2. After separation the organic layer was washed with 50 ml of H_2O (twice), dried on $MgSO_4$, and filtered. After evaporation of the solvent the residue was recrystallised from ethanol. Yields 57–64%.

b 1.6 mmol of the appropriate phosphineoxide was suspended in 10 ml of toluene. Then 1.0 g (7.04 mmol) of (i-Bu_2)AlH was added dropwise under vigorous stirring; the solid disappeared. The solution was stirred at room temperature for 0.5 h, followed by 0.5 h at 70 °C and two hours at reflux temperature. Upon cooling to 0 °C 5 ml of ethanol was added dropwise. After addition of 10 ml of H_2O and 10 ml of 4 n NaOH in H_2O, the mixture was vigourously shaken for five minutes. After separation, the organic layer was washed twice with 10 ml of H_2O and dried on $MgSO_4$. After filtration and evaporation of the solvent, the product was recrystallised from ethanol. Yields 62–70%.

Preparation of [Rh(COD)($\widehat{P\,P}$)]$^+$[ClO_4]$^-$ (7–9)

0.1831 mmol of 70% $HClO_4$ was added to a solution of 0.185 mmol of Rh(COD)acac in 50 ml of THF. The colour changed from light yellow to light orange. Subsequently, a solution of 0.1757 mmol of the appropriate diphosphine in 50 ml of THF was added dropwise in about three hours under vigorous stirring.

Stirring was continued for one hour. Upon concentration to 5 ml the product was precipitated by slow addition of diethyl ether and isolated by filtration. The complexes were recrystallised by dissolution in a minimal amount of CH_2Cl_2 and addition of an equal volume of ethanol. Stepwise addition of diethyl ether was required to complete crystallisation. Yields 70–90%.

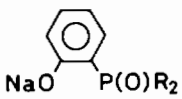
Reaction of $[Rh(COD)(\widehat{P\ P})]^+[ClO_4]^-$ with CO (10–12)

CO gas was bubbled through a solution of about 100 mg of the appropriate $[Rh(COD)(\widehat{P\ P})][ClO_4]$ complex in 3 ml of $CH_2Cl_2/CDCl_3$ (2:1) for five minutes. The colour changed from dark red-brown to dark orange. The solution thus obtained was used for NMR measurements.

Results and Discussion

Diphosphinedioxides and Diphosphines (Fig. 1)

The diphosphinedioxides (**1–3**) have been prepared in high yields (80–90%) via reaction of two equivalents of the appropriate



with di- or triethylene glycol ditosylate.

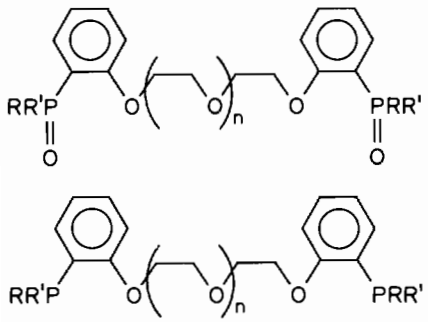


Fig. 1. Diphosphinedioxides: 1 R, R′ = Ph n = 1; 2 R, R′ = Ph n = 2; 3 R = Ph n = 1; R′ = Me. Diphosphines: 4 R, R′ = Ph n = 1; 5 R, R′ = Ph n = 2; 6 R = Ph n = 1; R′ = Me.

For the preparation of the corresponding diphosphines (**4–6**) by reduction of the diphosphinedioxides, two methods have been employed. Reduction with Si_2Cl_6 (method a) or with diisobutylaluminium hydride (method b), followed by hydrolysis, give comparable yields (60–70%). In their solid form **4–6** are stable; in solution only **6** is sensitive to air. Compounds **1–6** are spectroscopically characterised. The NMR data are given in Tables I and II. In the case of **3** and **6** racemic mixtures are obtained. In the ^{31}P-NMR of **6** two signals are found, attributable to the two diastereomers.

$[Rh(COD)(\widehat{P\ P})][ClO_4]$ Complexes

Reaction between Rh(COD)acac, $HClO_4$ and the appropriate diphosphine gives in moderate yields the *cis*-$[Rh(COD)(\widehat{P\ P})][ClO_4]$ complexes. In general a mixture of various species is obtained, as described previously for the $Ph_2PCH_2CH_2(OCH_2CH_2)_nPPh_2$ analogues (n = 1,2,3) [3]. Apparently, the resulting $[Rh(COD)(\widehat{P\ P})][ClO_4]$ complexes are not very stable and tend to lose COD. This is supported by the observation that on recording the NMR spectrum, gradually more signals arise, due to slow decomposition in $CDCl_3$.

The ^{31}P-NMR parameters of the complexes are shown in Table III. We have only tabulated the main signals. For **7–9** in each of the three cases a doublet is observed, which we assign to arise from a monomeric species (**7a–9a**), the structure of which is shown in Fig. 2.

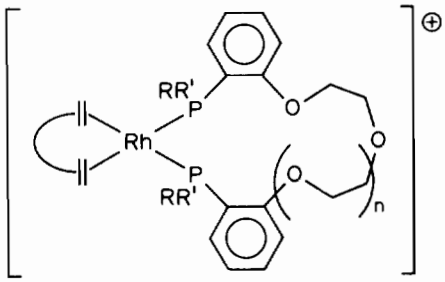
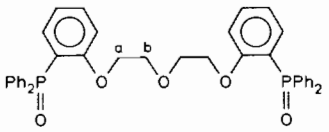
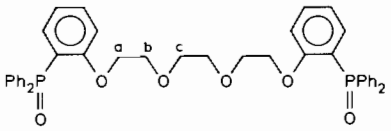
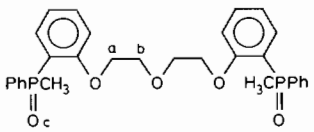
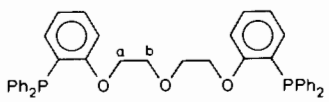
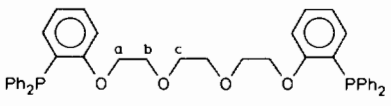
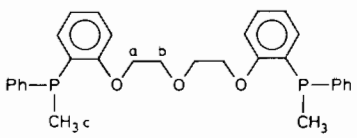


Fig. 2. Proposed structure of $[Rh(COD)(\widehat{P\ P})][ClO_4]$: **7a** R, R′ = Ph n = 1; (**8a** R, R′ = Ph n = 2); **9a** R = Ph R′ = Me n = 1.

It is noticeable that the ^1J(Rh–P) couplings for **7a–9a** differ considerably, *viz.* 128.78 Hz, 170.90 Hz and 144.04 Hz, respectively. This difference may point to a difference between the three ligands with regard to interaction of the ether oxygens with the metal centre. For the analogous $[Rh(COD)(Ph_2PCH_2CH_2(OCH_2CH_2)_nPPh_2)][ClO_4]$ (n = 1–3) complexes we have found a ^1J(Rh–P) coupling of about 144 Hz [3].

In the ^{31}P-NMR spectrum of **7** two quartets are observed as well, arising from a species b, with two unequivalent phosphino groups in cis-position to each other as can be seen from the ^2J(P–P) value of 22.58 Hz. The two ^1J(Rh–P) values (of 117.80 and of 120.24 Hz) indicate that the Rh-centre is not four-coordinate. The high downfield shifts of 43.00 and 53.53 ppm, respectively, point out that both P nuclei and therefore also the metal centre are less electron-rich. We think that **7b** has lost the COD ligand, because chemical analysis of an unpurified sample evidently shows lower C and H percentages. Moreover, in the ^{1}H-NMR spectrum the olefine signals are entirely absent. The absence of COD is further confirmed by the fact that **7b** does not react with CO at all. The proposed structure with all three ether oxygens coordinated is shown in Fig. 3.

TABLE I. ^{1}H- and ^{31}P-NMR Data of the Diphosphinedioxides and Diphosphines. Spectra measured in $CDCl_3$.

Number	Compound	^{1}H NMR	$^{31}P\{^{1}H\}$ NMR
1	 m.p. 158–160 °C	δ(a) = 3.79 t (4 H) δ(b) = 3.05 t (4 H) δ(arom) = 6.8–7.9 m (28 H)	δP = +26.46
2	 m.p. 131–133 °C	δ(a) = 3.92 t (4 H) δ(b) = 3.22 t (4 H) δ(c) = 3.31 s (4 H) δ(arom) = 6.8–8.0 m (28 H)	δP = +26.29
3	 (R, S)$_P$ m.p. 138–140 °C	δ(a) = 4.00 m (4 H) δ(b) = 3.59 t (4 H) δ(c) = 2.07 d; J(P) = 14.04 (6 H) δ(arom) = 6.8–8.1 m (18 H)	δP = +28.32
4	 m.p. 126–127 °C	δ(a) = 3.86 t (4 H) δ(b) = 3.34 t(4 H) δ(arom) = 6.7–7.3 m (28 H)	δP = –15.48
5	 m.p. = 117–118 °C	δ(a) = 4.02 t (4 H) δ(b) = 3.49 t (4 H) δ(c) = 3.29 s (4 H) δ(arom) = 6.6–7.8 m (28 H)	δP = –15.41
6	 (R, S)$_P$ m.p. 111–113 °C	δ(a) = 4.01 m (4 H) δ(b) = 3.64 m (4 H) δ(c) = 1.60; J(P) = 3.79 (6 H) δ(arom) = 6.8–7.5 m (18 H)	δP = –34.84, –34.89

Reaction of [Rh(COD)(P⌒P)][ClO$_4$] with CO

In order to examine the coordination behaviour of the diphosphines upon displacement of the *cis*-coordinated COD ligand, we have reacted complexes **7a**–**9a** with CO, yielding **10**–**12**.

As seen from Table III, ^{1}J(Rh–P) for the CO-

TABLE II. ^{13}C-NMR Data of the Diphosphines. Spectra measured in $CDCl_3$.

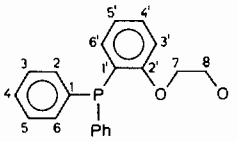
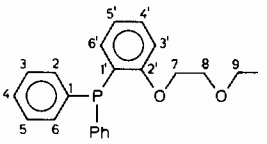
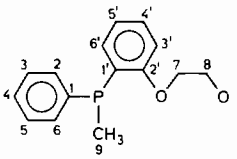
Number	Compound	δ(C)	*J*(P)
4		$\delta(C_1) = 136.76$ $\delta(C_2) = 133.87$ $\delta(C_3) = 128.21$ $\delta(C_4) = 128.40$ $\delta(C_1') = 126.11$ $\delta(C_2') = 160.14$ $\delta(C_3') = 111.21$ $\delta(C_4') = 130.03$ $\delta(C_5') = 121.01$ $\delta(C_6') = 133.30$ $\delta(C_7) = 69.28$ $\delta(C_8) = 68.01$	$J(P) = 11.03$ $J(P) = 20.22$ $J(P) = 7.35$ $J(P) = 0$ $J(P) = 12.90$ $J(P) = 14.30$ $J(P) = 1.49$ $J(P) = 0$ $J(P) = 0$ $J(P) = 0$
5		$\delta(C_1) = 136.73$ $\delta(C_2) = 133.87$ $\delta(C_3) = 128.24$ $\delta(C_4) = 128.47$ $\delta(C_1,) = 126.12$ $\delta(C_2') = 160.14$ $\delta(C_3') = 111.21$ $\delta(C_4') = 130.08$ $\delta(C_5') = 121.14$ $\delta(C_6') = 133.33$ $\delta(C_7) = 69.12$ $\delta(C_8) = 68.19$ $\delta(C_9) = 70.68$	$J(P) = 10.66$ $J(P) = 20.22$ $J(P) = 7.35$ $J(P) = 0$ $J(P) = 12.87$ $J(P) = 14.71$ $J(P) = 1.47$ $J(P) = 0$ $J(P) = 0$ $J(P) = 0$
6		$\delta(C_1) = 139.61$ $\delta(C_2) = 132.39$ $\delta(C_3) = 128.10$ $\delta(C_4) = 128.18$ $\delta(C_1') = 129.27$ 128.56 $\delta(C_2') = 160.05$ $\delta(C_3') = 111.21$ $\delta(C_4') = 129.69$ $\delta(C_5') = 120.94$ $\delta(C_6') = 131.71$ $\delta(C_7) = 69.48$ $\delta(C_8) = 67.72$ $\delta(C_9) = 11.02$	$J(P) = 11.40$ $J(P) = 19.49$ $J(P) = 6.99$ $J(P) = 0$ $J(P) = 18.75$ 13.60 $J(P) = 12.13$ $J(P) = 1.10$ $J(P) = 0$ $J(P) = 2.57$ $J(P) = 6.25$ $J(P) = 12.87$

TABLE III. $^{31}P\{^1H\}$NMR Data of Rh(I)diphosphino–(poly)ether Complexes. Measured in $CDCl_3$.

		δP	^1J(Rh–P)	^2J(P–P)*cis*
7a	[Rh(COD) (4)][ClO_4]	25.95	128.78	
7b	see text	43.00(P1)	117.80	22.58
		53.53(P2)	120.24	22.58
10	[Rh(CO) (4)][ClO_4][a]	19.25	105.59	
8a	[Rh(COD) (5)][ClO_4]	31.62	170.90	
11	[Rh(CO) (5)][ClO_4][b]	28.16	152.90	
9a	[Rh(COD) (6)][ClO_4]	1.47	144.04	
12	[Rh(CO)(6)][ClO_4][c]	6.58	127.23	

[a] ν(CO) = 1977 vs. [b] ν(CO) = 1973sh, 2005m. [c] ν(CO) = 2025s, 1968m.

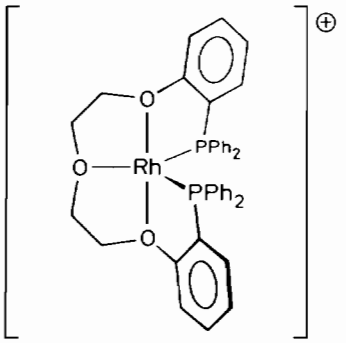


Fig. 3. Proposed structure of **7b**.

complex is 17–23 Hz lower than ^1J(Rh–P) for the corresponding COD complex. For the analogous $[Rh(CO)(Ph_2PCH_2CH_2OCH_2CH_2PPh_2)][ClO_4]$ we have found a decrease of ^1J(Rh–P) of 15 Hz in comparison with the value of ^1J(Rh–P) for $[Rh(COD)(Ph_2PCH_2CH_2OCH_2CH_2PPh_2)][ClO_4]$ [5]. Determination of the X-ray structure of the former compound by Alcock *et al.* has revealed trans-coordination of CO and the ether oxygen [6]. For this complex we have observed ν(CO) at 1974 cm^{-1}. Also because we find ν(CO) for **10–12** in the same range, we propose a structure similar to that determined by Alcock, which is shown in Fig. 4.

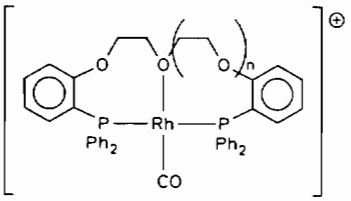


Fig. 4. Proposed structure of **10–12**: **10** R, R' = Ph n = 1; **11** R, R' = Ph n = 2; **12** R = Ph R' = Me n = 1.

Acknowledgements

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