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Chiral diphospholes

III *. Improved synthesis and coordination chemistry of (*R,R*)-DIPPOP

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Abstract

An improved, 90% yield synthesis of the chiral diphosphole, (*R,R*)-DIPPOP (**1**) is reported. The reactions of **1** with nickel, palladium, platinum and rhodium complexes are examined. **1** does not react with $NiCl_2$. With $PdCl_2$ and $PtCl_2$, it forms various *cis* and *trans* diphosphine-bridged cyclooligomers of undetermined ring size. The rhodium complexes $[Rh(cod)_2]BF_4$, [Rh(acac)(cod)] and $\{Rh(\mu\text{-Cl})(cod)\}_2$ are good precursors for the synthesis of [Rh(cod){(*R,R*)-DIPPOP}]BF_4, (**8**), [Rh(acac){(*R,R*)-DIPPOP}], (**9**), and $\{Rh(cod)Cl\}_2\{\mu\text{-P,P'-}(R,R)\text{-DIPPOP}\}$, (**10**), which are fully characterized by multinuclear NMR spectroscopy.

1. Introduction

We previously showed that phospholes are better ligands than the conventional triphenylphosphine in the rhodium-catalysed hydrogenation [1] and hydroformylation [2] of various unsaturated substrates. As part of a programme on the synthesis of chiral phospholes and their use in enantioselective catalysis, we hoped to prepare chiral diphospholes by replacing the commonly-used PPh_2 groups [3] by the phosphol-1-yl moieties.

Some chiral diphospholes are already known with the dibenzophosphol-1-yl moieties [4], and they do not behave like typical phospholes [5].

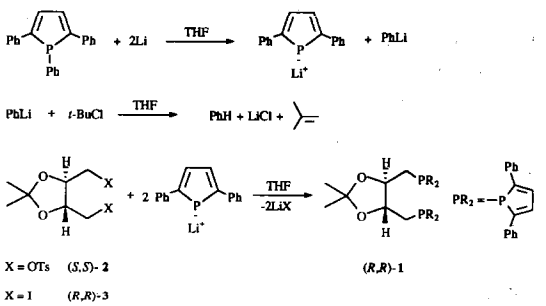
We recently described the synthesis of the DIOP analogues bearing the 2,5-diphenylphosphol-1-yl groups, *i.e.* (2*R*,3*R*)- and (2*S*,3*S*)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(2,5-diphenylphosphol-1-yl)-butane, abbreviated (*R,R*)- and (*S,S*)-DIPPOP, (**1**) in 34–44% yields [6]. Preliminary results on the synthesis of two (*R,R*)-DIPPOP rhodium complexes and their evaluation in enantioselective catalytic hydrogenation were also reported [7]. We now report an improved synthesis of (*R,R*)-DIPPOP and the exploration of the classical reactions to form complexes with platinum-group metals of interest in catalysis.

2. Results and discussion

2.1. Improved synthesis of (R,R)-DIPPOP

The synthesis of (*R,R*)-DIPPOP, (*R,R*)-**1**, extrapolated from the synthesis of DIOP described by Kagan and Dang [8], is outlined in Scheme 1.

Generation of the 2,5-diphenylphospholyl anion by lithium cleavage of the exocyclic phosphorus–carbon bond of 1,2,5-triphenylphosphole also produces phenyllithium which may compete with the phospholyl anion



Scheme 1.

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* For Parts 1 and 2 see refs. 6 and 7 respectively.

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during the S_N2 reaction on the ditosylate (*S,S*)-**2**. Therefore, it was selectively destroyed using tert-butyl chloride. The destruction of phenyllithium is a slow reaction, requiring more than 2 h and up to 12 h has been used under our reaction conditions, before adding (*S,S*)-**2**. An isolated yield of 90% after purification by liquid chromatography, *versus* 44% [6], was achieved for (*R,R*)-**1**.

2.2. Attempted synthesis of a nickel complex

As 1,2,5-triphenylphosphole, which does not form a complex with $NiCl_2$ [9], (*R,R*)-**1** does not react with $NiCl_2 \cdot 6H_2O$ in refluxing ethanol.

2.3. Synthesis of palladium complexes

The reaction was attempted of **1** with $[PdCl_2(MeCN)_2]$, $[PdCl_2(PhCN)_2]$, and $[PdCl_2(cod)]$, which are well-known precursors for the synthesis of $[PdCl_2(phosphine)_2]$ and $[PdCl_2(diphosphine)]$ [10–12].

$[PdCl_2(MeCN)_2]$ reacts with **1** in benzene to give an orange solid after precipitation with pentane. ^{31}P NMR analysis showed it to be a mixture containing one main complex (**4**, $\delta^{31}P = 19$ ppm).

$[PdCl_2(PhCN)_2]$ was treated with **1** in refluxing acetone as reported for the synthesis of the complex $[PdCl_2\{(S,S)\text{-DIOP}\}]$ [13]. An orange solid precipitated, mainly complex **4**, and the same by-products as with $[PdCl_2(MeCN)_2]$ (^{31}P NMR analysis). Complex **4** was isolated pure, albeit in moderate yield (33%), using more dilute solutions at room temperature.

In contrast, the reaction of $[PdCl_2(cod)]$ with **1** in acetone gave rise to **4** as the sole product isolated in good yield (77%).

The elemental analysis of **4** is consistent with a product containing $PdCl_2$ and **1** in a 1:1 ratio. The ^1H NMR spectrum is not informative. Unfortunately, we could not obtain the ^{13}C NMR spectrum owing to the poor solubility and the decomposition of **4** in $CDCl_3$. The IR spectrum (KBr pellet) exhibits a single ν(Pd–Cl) absorption at 360 cm^{-1} suggestive of a *trans* square-planar arrangement around the palladium atom in the solid state [12,14–16]. In solution, the observed ^{31}P chemical shift (19 ppm) is consistent with a *cis* structure [17,18]. However, the ^{31}P resonances of phospholes are shifted downfield relative to normal phosphines and phosphole complexes that exhibit the same ^{31}P shifts as **1** are *trans* with shifts around 20 ppm [19]. The occurrence of phosphine palladium complexes with a *trans* configuration is unusual, and, in most cases a *cis* configuration is more stable. However, bulky phosphines favour a *trans* configuration [12]. Examination of molecular models showed that **1** is very crowded and thus may preferentially give *trans* arrangements. On the basis of these data, it is suggested that complex **4** is one (or a mixture of) *trans*-diphosphine-bridged cyclooligomer(s) of unknown ring size (eqn. (1)).

$$n[PdCl_2(cod)] \text{ or } n[PdCl_2(PhCN)_2] + n(R,R)\text{-DIPPOP} \xrightarrow{\mathbf{1}} [\mathit{trans}\text{-}PdCl_2\{(R,R)\text{-DIPPOP}\}]_n + \underset{2n\,PhCN}{\overset{n\,COD}{\text{or}}} \quad (1)$$

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2.4. Synthesis of platinum complexes

The reaction of **1** was attempted with $[PtCl_2(PhCN)_2]$ or $[PtCl_2(cod)]$ which are well-known precursors for the synthesis of $[PtCl_2(phosphine)_2]$ and $[PtCl_2(diphosphine)]$ [20].

Depending on the experimental conditions, the reactions of **1** with $[PtCl_2(PhCN)_2]$ leads to a mixture of at least four products (^{31}P NMR analysis). All give single lines accompanied by ^{195}Pt satellites at $\delta^{31}P$ = 15.2, 16.1, 16.9 and 18.2 ppm, the coupling constants $^1J(^{31}P-^{195}Pt)$ being in the range 2445–2472 Hz. Under proper conditions (see Experimental section), it has been possible selectively to prepare and to isolate two of these complexes, **5** [$\delta^{31}P = 16.1$ ppm; $^1J(^{31}P-^{195}Pt) = 2456$ Hz] and **6** [$\delta^{31}P = 18.2$ ppm; $^1J(^{31}P-^{195}Pt) = 2447$ Hz]. In both cases, elemental analysis is consistent with a 1:1 adduct between $PtCl_2$ and **1**. Complexes **5** and **6** are very poorly soluble in conventional organic solvents. The IR spectra (KBr pellet) exhibit only one absorption for ν(Pt–Cl) at 350 cm^{-1} and the values of the $^1J(^{31}P-^{195}Pt)$ coupling constants are as expected for *trans* $[PtCl_2(phosphine)_2]$ [16–18]. Like the palladium complexes, all the complexes generated in this reaction, including **5** and **6**, are believed to be *trans* diphosphine-bridged cyclooligomers (eqn. (2)).

$$n[PtCl_2(PhCN)_2] + n(R,R)\text{-DIPPOP} \xrightarrow{\mathbf{1}} [\mathit{trans}\text{-}PtCl_2\{(R,R)\text{-DIPPOP}\}]_n + 2n\,PhCN \quad (2)$$

5, **6**, *etc.*

The course of the reaction of **1** with $[PtCl_2(cod)]$ is different. It afforded very selectively (in CH_2Cl_2 or acetone at room temperature) or exclusively (acetone at 0°C) the complex **7** [$\delta^{31}P = 0.2$ ppm; $^1J(^{31}P-^{195}Pt) = 3210$ Hz]. Elemental analysis also implies a 1:1 complex between $PtCl_2$ and **1**. The low solubility of **7** precludes ^1H and ^{13}C NMR spectroscopy and molecular-weight determination. IR analysis (CsBr pellet) shows two ν(Pt–Cl) absorptions at 291 and 314 cm^{-1},

TABLE 1. ^{31}P and ^{1}H NMR data ($CDCl_3$) of complexes **8**, **9** and **10** as compared to those of **1** and (*R*,*R*)-DIOP [a]

	^{31}P NMR δ(ppm)[^{1}J(P–Rh)]	^{1}H NMR [c]	$H^{1'}$	$H^{2'}$	$H^{4'}$	H^{3}	H^{5}	$H^{6}+H^{7}$	H^{a}	$H^{v,v'}$	H^{α}	H^{γ}
(*R*,*R*)-DIOP	−22.5	δ	2.3(m)	3.8(m)	1.28(s)		7.1–7.3(m)					
[Rh(cod){(*R*,*R*)-DIOP}]BF_4	12.7(145) $\Delta\delta^{31}P = 35.2$ [b]	δ	2.1–2.7(m)	3.6(m)	1.1(s)		7.5–7.8(m)		2.1–2.7(m)	4.5(bs)		
		δ [d]	1.65(d) [f] 1.78(d) [f]	3.39(bm)	1.10(s)	7.11(s)	7.48(bs)	7.20–7.40(m)				
1	−8.3	J(H–P) [e]	2.5 [g] 4.1 [g]		0	10						
		J(H–H) [d]	3.2 8.6		–	–						
8	18.7(133) $\Delta\delta^{31}P = 27$ [b]	δ	1.9–2.7(m)	3.32(m)	0.82(s)	7.0–7.7(m)	7.8–8.2(m)	7.0–7.7(m)	1.9–2.7(m)	4.88(m) 5.46(m)		
9	49.2(176)	δ	1.7–2.0(m)	3.10(m)	0.80(s)	6.7–7.5(m)	8.28(d) 8.41(d)	6.7–7.5(m)			1.63(s)	5.25(s)
	$\Delta\delta^{31}P = 57.5$ [b]	J(H–H) [d]					7 7					
10	24(135)	δ [d]	1.70–2.50(m)	2.98(m) [h]	0.41(s)	6.94(d) 6.95(d)	7.86(pd) 7.94(pd)	7.18–7.41(m)	1.70–2.50(m)	3.09(bs) 5.51(bs)		
	$\Delta\delta^{31}P = 32.3$ [b]	J(H–P) [e]		6	0	22 22	0 0					
		J(H–H) [d]				19 19	7 7					

[a] Bruker WM 250; abbreviations: b: broad; d: doublet; m: multiplet; p: pseudo; s: singlet; t: triplet; δ in ppm and J in Hz. [b] Coordination chemical shift = δ(complex) − δ(phosphane). [c] Numbering is found in the equations. Unbound and complexed phospholes have the same numbering. DIOP and complexed DIOP have the same numbering as DIPPOP including the hydrogen atoms of the PPh_2 substituent designated H^5 and H^6+H^7. [d] $^{1}H\{^{31}P\}$ NMR. [e] ^{1}H NMR. [f] $^{1}H\{^{31}P, H^{2'}\}$ NMR; ^{2}J(H–H) = 14 Hz. [g] $^{1}H\{H^{2'}\}$ NMR. [h] Unresolved AB type spectrum.

consistent with a *cis* square-planar arrangement around the platinum atom [16]. The $^1J(^{31}P-^{195}Pt)$ coupling constant, above 3000 Hz, is also consistent with such a structure [16–18]. We thus conclude that **7** is either the chelate complex (**7**, $n = 1$) or a *cis* diphosphine-bridged cyclooligomer (eqn. (3)).

$$n[PtCl_2(cod)] + n(R,R)\text{-DIPPOP} \xrightarrow{\mathbf{1}} [cis\text{-}PtCl_2\{(R,R)\text{-DIPPOP}\}]_n + n\text{COD} \quad (3)$$

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The degree of cyclooligomerization of complexes **4–7** is not known but dimeric or trimeric structures have been proposed for similar complexes [4g,21].

It is generally assumed that only monomeric complexes are formed by reaction of a diphosphine with a palladium or a platinum precursor. The results of the present study clearly indicate that care must be exercised with such assumptions.

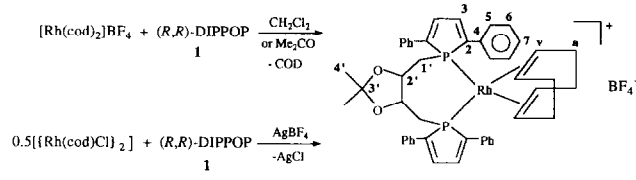
2.5. Synthesis of rhodium complexes

The chemistry of **1** was explored with $[Rh(cod)_2]BF_4$, [Rh(acac)(cod)] and $[\{Rh(\mu\text{-Cl})(cod)\}_2]$ by classical procedures in order to examine and compare the resulting complexes with their DIOP analogues.

2.6. Reaction of 1 with $[Rh(cod)_2]BF_4$

Following the synthesis of the complex [Rh(cod)-{(*R*,*R*)-DIOP}]BF_4 [22], the reaction of **1** with $[Rh(cod)_2]BF_4$ or $[\{Rh(cod)Cl\}_2] + AgBF_4$ afforded the chelate complex **8** (68%) (Scheme 2).

Complex **8** was identified by elemental analysis and multinuclear NMR spectroscopy. The ^1H and ^{31}P NMR data of **1** and **8** are gathered in Table 1, together with



Scheme 2.

those of (*R*,*R*)-DIOP and [Rh(cod){(*R*,*R*)-DIOP}]BF_4 which have been prepared for comparison [22]. It appears that the coordination chemical shift, $\Delta\delta^{31}P$, is smaller for **8** than for the analogous (*R*,*R*)-DIOP complex. Such a difference has already been observed in the coordination chemistry of phospholes and attributed to significant backbonding to the phospholyl ring [9,23]. This explanation is supported by the ^1H NMR data. The resonances of the cod vinylic hydrogen atoms, H^v, appear at lower field for **8** than for [Rh(cod){(*R*,*R*)-DIOP}]BF_4.

Carbon 13 NMR data for **8** and for (*R*,*R*)-DIPPOP are given in Table 2. In the $^{13}C\{^1H\}$ NMR spectrum of **8**, the resonances of C^2, C^3, C^4, C^5, $C^{1'}$ and $C^{2'}$ are all pseudo-triplets due to AXX′ spin systems (A = ^{13}C, X = X′ = ^{31}P). According to the analysis of this spin system [24,25], the $^2J(P-P)$ coupling is small (~ 10 Hz) and the coupling constants $^1J(C-P)$ and $^3J(C-P)$ have opposite signs. For all these carbon atoms, the observed figures never are the actual triplets which would arise from a large $^2J(P-P)$ coupling constant (> 50 Hz). These data demonstrate the *cis* arrangement of two phosphorus atoms around the rhodium (Scheme 2).

TABLE 2. ^{13}C NMR data ($CDCl_3$) of complexes **8**, **9** and **10** as compared to those of **1** and cod ($\delta C^a = 28.5$; $\delta C^{v,v'} = 128.5$ ppm) [a]

	Carbons [b]	$C^{1'}$	$C^{2'}$	$C^{3'}$	$C^{4'}$	C^2	C^3	C^4	C^5	C^6	C^7	C [a]	$C^{v,v'}$	C^α	C^β	C^γ
1	δ [c]	28.7	78.9	109.6	26.9	152.0(b)	132.0	136.7(b)	126.6	128.7	127.1					
	(ppm)					152.3(b)		137.1(b)								
	$\lvert J(C-P)\rvert$ [d]	17	~ 0	~ 0	0	~ 0	~ 0	17(bd)	9(d)	0	0					
	(Hz)(mult.)							17(bd)								
8	δ [c]	32.00	75.20	109.22	26.24	148.00	136.73	132.71	127.60	129.57	129.65	26.59	103.72 [e]			
	(ppm)					149.14	137.51	134.72	127.75	129.65	129.98	35.83	104.98 [e]			
	$\lvert J(C-P)\rvert$ [d]	14(pt)	3(pt)	0	0	~ 17(pt)	5(pt)	7(pt)	3(pt)	0	0	0	6			
	(Hz)(mult.)					~ 22(pt)	5(pt)	7(pt)	3(pt)	0	0	0	3			
9	δ [c]	33.5	76.3	107.6	26.4	149.3	132.6	136.5	n.a.	n.a.	n.a.			30.2	184.9	99.6
	(ppm)					153.0	132.7	137.6							186.6	
	$\lvert J(C-P)\rvert$ [d]	14(pt)	n.a.	0	0	17(pt)	~ 5(m)	7(pt)						0	0	0
	(Hz)(mult.)					21(pt)	~ 5(m)	7(pt)								
10	δ [c]	26.30	77.42	109.00	26.47	144.12	132.49	133.55	126.92	128.42	127.79	29.00	74.06 [f]			
	(ppm)					147.44	133.92	134.90	127.48	129.10	128.37	32.66	103.07 [g]			
	$\lvert J(C-P)\rvert$ [d]	20(d)	9(pt)	0	0	38(d)	10(d)	14(d)	7(d)	0	0	0	0			
	(Hz)(mult.)					37(d)	10(d)	14(d)	7(d)	0	0	0	11(d)			

[a] See footnote a, Table 1; n.a. not assigned. [b] Numbering is found in the equations. Unbound and complexed phospholes have the same numbering. [c] $^{13}C\{^1H,^{31}P\}$ NMR. [d] $^{13}C\{^1H\}$ NMR. [e] d, $^1J(^{13}C-^{103}Rh) = 7$ Hz. [f] $^1J(^{13}C-^{103}Rh) = 13$ Hz. [g] $^1J(^{13}C-^{103}Rh) = 8$ Hz.

The phosphorus-decoupled $^{13}C\{^1H\}$ spectrum of **8** shows that the vinylic carbon atoms of cod are magnetically nonequivalent in pairs and give rise to two doublets [$^1J(^{13}C-^{103}Rh) = 7$ Hz]. This value is somewhat smaller than those general reported for olefin-rhodium complexes [$^1J(^{13}C-^{103}Rh) = 10$–$16$ Hz] [24]. The allylic carbon atoms are also magnetically nonequivalent in pairs. The coordination chemical shifts $\Delta\delta^{13}C^v = -24.5$ to -24.8 and $\Delta\delta^{13}C^a = -1.9$ to 7.3 (resonances for uncoordinated cyclooctadiene at $\delta C^v = 128.5$ and $\delta C^a = 28.5$ ppm [26]) are close to the values reported for analogous [Rh(cod)(diphosphine)]$^+$ complexes [27]. These values are consistent with either a boat [27] or a twist-boat conformation of the cod ligand [28]. The resonances of carbon atoms $C^{1'}$, $C^{2'}$, $C^{3'}$ and $C^{4'}$ of the chiral carbon backbone are singlets. Those of carbon atoms C^2 and C^3 of the phospholyl ring and C^4 to C^7 of aromatic rings are all doublets. Thus, carbon atoms C^2, C^3, C^4, C^7 and C^5, C^6 are magnetically nonequivalent in pairs and in fours, respectively. This reflects a symmetrical rigid conformation of a rhodadiphosphacycloheptane arrangement. The coordination of (*R*,*R*)-DIPPOP induces a downfield shift and an upfield shift of C^2 and C^3 carbon atom resonances, respectively, as well as an increase of the J(C–P) coupling constants. Similar observations have already been reported in the case of 3,4-dimethyl-1-phenylphosphole and attributed to a polarization of the C^2–C^3 bond [29].

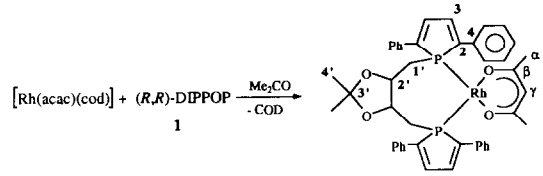
2.7. Reaction of 1 with [Rh(acac)(cod)]

It has been reported that cationic complexes [Rh(cod){(*R*,*R*)-DIOP}]A (A = BF_4 (BPh_4) can be prepared by reaction of [Rh(acac)(cod)] with (*R*,*R*)-DIOP in the presence of $NaBF_4$ or $NaBPh_4$ (eqn. (4)) [30].

$$[Rh(acac)(cod)] + (R,R)\text{-DIOP} \xrightarrow[EtOH/MeOH]{NaBF_4 \text{ or } NaBPh_4} [Rh(cod)\{(R,R)\text{-DIOP}\}]A \quad (4)$$

This reaction to displace the acac seemed a valuable alternative to previous methods for the synthesis of cationic rhodium complexes since it avoids the use of silver salts or of strong acids (*e.g.* $HClO_4$ and HBF_4). However, when trying to repeat it we obtained a mixture of products (^{31}P NMR analysis) one of which [$\delta^{31}P = 12$ ppm; $^1J(P-Rh) = 144$ Hz] is the expected [Rh(cod){(*R*,*R*)-DIOP}]A.

Surprisingly, the reaction of **1** with [Rh(acac)(cod)] in the presence of either $NaBF_4$ or $NaBPh_4$ gave only one complex, [Rh(acac){(*R*,*R*)-DIPPOP}] (**9**) [$\delta^{31}P = 49.2$ ppm; $^1J(P-Rh) = 176$ Hz] by substitution of the cod and not the acac. This complex is best prepared by mixing the rhodium precursor and **1** in acetone at room temperature (*i.e.* without $NaBF_4$ or $NaBPh_4$) (Scheme 3).



1 **9**

Scheme 3.

Elemental analysis, ^1H and ^{13}C NMR data are in agreement with the proposed formula. In addition to the resonances of coordinated **1**, the ^1H NMR spectrum exhibits the resonances of the acac which is *O*,*O*-coordinated (Table 1). $^{13}C\{^1H\}$ and $^{13}C\{^1H,^{31}P\}$ NMR data (Table 2) are similar to those of **8**. Specifically, the resonances of carbon atoms C^2, C^3 and C^4 are characteristic of AXX′ spin systems and thus consistent with a *cis* arrangement of 2 phosphorus atoms around the rhodium (Scheme 3).

Complex **9** is a rare examples of complexes of general formula [Rh(X-Y)(P-P)] (X-Y = bidentate monoanionic ligand; P-P = bidentate neutral ligand) [31] and, to the best of our knowledge, the first involving a chiral diphosphine. Although complexes [Rh(acac)$(PR_3)_2$] have been known for 20 years [32], the only one containing a diphosphine, [Rh(5-methyl-8-hydroxyquinolato){(*cis*-1,2-diphenylphosphino)ethylene}], was described in 1981 [33]. Several complexes of this series, [Rh(acac)(P-P)] and [Rh(dpm)(P-P)] (dpm = dipivaloylmethanato; P-P = dppm, dppe, dppp, *etc.*), were recently reported [34]. They exhibit typically a large ^1J(P–Rh) coupling constant (~ 190 Hz), as is the case for **9** as compared with **8**.

2.8. Reaction of 1 with [{Rh(μ-Cl)(cod)}$_2$]

The complex [{Rh(μ-Cl)(cod)}$_2$] is also a precursor for the synthesis of cationic rhodium complexes of (*R*,*R*)-DIOP (eqn. (5)) [30].

$$0.5[\{Rh(\mu\text{-}Cl)(cod)\}_2] + (R,R)\text{-DIOP} \xrightarrow[MeOH]{NaBPh_4} [Rh(cod)\{(R,R)\text{-DIOP}\}]BPh_4 \quad (5)$$

A similar reaction conducted with **1** gave a mixture of two complexes [$\delta^{31}P = 18$ ppm; $^1J(P-Rh) = 133$ Hz and $\delta^{31}P = 24$ ppm; $^1J(P-Rh) = 135$ Hz]. The first is probably the BPh_4^- analogue of **8** (^{31}P NMR analysis). Interestingly, the second one, **10**, could be prepared selectively from the reaction of **1** (2 equiv) with [{Rh(cod)Cl}$_2$] (1 equiv) in acetone (*i.e.* in the absence of $NaBPh_4$) (eqn. (6)).

According to the stoichiometry of the reaction, half the amount of (*R*,*R*)-DIPPOP should have been recovered. After isolating **10**, we recovered a solid of the

expected weight. The ^{31}P NMR spectrum of this material showed several signals, none of them corresponding to unreacted **1**, indicating that **1** has been oxidized or transformed into as yet unidentified compounds.

$$[\{Rh(\mu\text{-Cl})(cod)\}_2] + (R,R)\text{-DIPPOP} \xrightarrow{Me_2CO} \underset{\mathbf{1}}{} \underset{\mathbf{10}}{[\{Rh(Cl)(cod)\}_2(R,R)\text{-DIPPOP}]} \quad (6)$$

As the complex was shown to contain traces of solvent (acetone, diethyl ether) which we could not eliminate (^1H NMR analysis), a satisfactory elemental analysis could not be obtained. The proposed formula and stereochemistry of complex **10** rest on the NMR data (Tables 1 and 2). The ^1H NMR spectrum clearly shows that complex **10** contains cyclooctadiene and **1** in a 2:1 ratio (integration of the cod vinylic resonances *vs.* the methyl resonances of **1**). Some other NMR features are as follows:

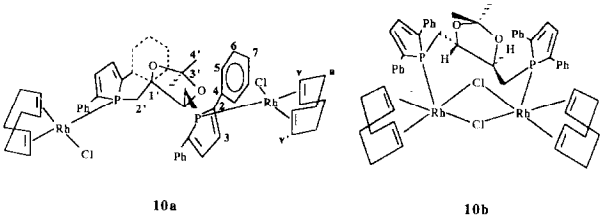
i) in the ^1H NMR spectrum, the $H^{4'}$ hydrogen atoms of the methyl groups resonate at 0.41 ppm. Such a high field resonance indicates that the methyl groups are symmetrically located in a shielded region of space.

ii) in the $^{13}C\{^1H\}$ NMR spectrum, unlike in **8** and **9**, the carbon atoms $C^{1'}$ and C^2 to C^5 give rise to doublets, consistent with only one phosphorus atom per rhodium.

On the basis of these data, **10** could be either **10a**, the product of cleavage of the chloro-bridges, or **10b**, the simple adduct of **1** and $[\{Rh(\mu\text{-Cl})(cod)\}_2]$ [35*] (Scheme 4).

Examination of molecular models shows that the only viable conformations for **10b** are those for which the methyl groups are not in a shielded region of space. We therefore favour structure **10a** which may adopt several conformations in which the methyl groups are symmetrically located in the shielded region of aromatic rings as drawn in Scheme 4.

The proposed stereochemistry, **10a**, is supported by the following observations. In the ^1H NMR spectrum, the resonances for the vinylic hydrogen atoms H^v and $H^{v'}$ are found at 5.51 and 3.09 ppm, respectively. This splitting indicates that the cyclooctadiene carbon-carbon double bonds are subjected to different *trans* influences. By comparison with the data reported for $[RhCl(cod)(PR_3)]$ [36], H^v and $H^{v'}$ are located *trans* to the phosphorus atom and *trans* to the chlorine atom, respectively. The $^{13}C\{^1H,^{31}P\}$ spectrum supports this proposal since the signals of carbon atoms C^v and $C^{v'}$ are found at 103.07 and 74.06 ppm respectively. The coupling constant $^1J(C^v\text{–}Rh)$, 8 Hz, is comparable to that determined for **8** [$^1J(C^v\text{–}Rh) = 7$ Hz] and the coupling constant $^1J(C^{v'}\text{–}Rh)$, 13 Hz, is comparable to that determined for $[\{Rh(\mu\text{-Cl})(cod)\}_2]$[$^1J(C^v\text{–}Rh) = 14$ Hz] [24a]. The $^{13}C\{^1H\}$ NMR spectrum shows that carbon atoms C^v, located *trans* to the phosphorus atoms, are coupled to phosphorus [$^2J(C^v\text{–}P) = 11$ Hz] whereas the carbon atoms $C^{v'}$, located *cis*, are not.



Scheme 4.

3. Conclusion

The chiral diphosphole, (*R,R*)-DIPPOP, belongs to the very large family of potential bidentate 1,4-diphosphines containing two achiral phosphorus atoms connected by a chiral carbon backbone. It gives rise to palladium, platinum, and rhodium complexes. With one possible exception, palladium and platinum adducts are cyclooligomers. In the case of rhodium, either monomers or dimers are formed depending on the rhodium precursor. This work emphasizes that chelate complexes of diphosphines do not readily form just by reaction of a diphosphine with a complex precursor, a method widely used for the preparation of the so-called *in situ* catalysts. This result may have some implications in catalytic reactions. Research is currently underway in the case of (*R,R*)-DIPPOP and other chiral diphospholes, and we will report our results in due course.

4. Experimental section

4.1. Methods and materials

All sample manipulations were under argon using standard Schlenk tube and vacuum techniques. Solvents and reagents were purified according to literature procedures [37] under argon and stored under argon. Argon U (L'Air Liquide) was used after passage through 3 Å molecular sieves. The complexes $[PdCl_2(PhCN)_2]$ [38], $[PdCl_2(cod)]$ [39], $[PtCl_2(PhCN)_2]$ [10], $[PtCl_2(cod)]$ [40], $[Rh(cod)_2]BF_4$ [41], [Rh(acac)(cod)] [42], and $[\{Rh(\mu\text{-Cl})(cod)\}_2]$ [43], and 1,2,5-triphenylphosphole [44] were prepared by published procedures.

* Reference number with an asterisk indicates a note in the list of references.

Infrared spectra were recorded using a Perkin-Elmer 597 spectrometer. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ solution on a Bruker WM 250 spectrometer. ^1H and ^{13}C NMR chemical shifts are referenced to tetramethylsilane assigning the solvent resonances at 7.27 and 77.0 ppm respectively. ^{31}P NMR chemical shifts are referenced to external 85% H_3PO_4 in D_2O. Elemental analyses were carried out by the Service Analyse du Laboratoire de Chimie de Coordination.

4.2. Improved synthesis of (R,R)-DIPPOP 1, (R,R)-1

The synthesis of **1** was carried out as previously described [6] except that the contact time with tert-butyl chloride was increased to at least 12 h. ^1H and ^{13}C NMR data have already been reported [6] but some of the ^{13}C NMR assignments were incorrect. The corrected ones are now given in Table 2.

4.3. Syntheses of the palladium complex 4

4.3.1. From $[PdCl_2(PhCN)_2]$

A solution of **1** (60 mg; 0.1 mmol) in acetone (2 ml) was added to a stirred solution of $[PdCl_2(PhCN)_2]$ (40 mg; 0.1 mmol) in acetone (2 ml). Acetone (20 ml) was added. After 15 min, a precipitate was formed which was filtered, washed with acetone and dried under reduced pressure to constant weight (25 mg).

4 (yield 33%). Found: C, 59.90; H, 4.73. $C_{39}H_{36}Cl_2O_2P_2Pd$ calc.: C, 60.37; H, 4.68%.

^1H NMR ($CDCl_3$): δ (ppm): 0.8, s, 6H, CH_3; 1.9–2.1, m, 4H, CH_2; 3.2, m, 2H, CH; 7.2–7.8, m, 24H, aromatic and phospholyl hydrogens.

4.3.2. From $[PdCl_2(cod)]$

A solution of **1** (60 mg; 0.1 mmol) in acetone (1 ml) was added to a stirred solution of $[PdCl_2(cod)]$ (28 mg; 0.1 mmol) in acetone (2 ml). The colour of the solution changed from yellow to orange while an orange solid precipitated. After 10 min, the precipitate was filtered, washed with acetone and dried under reduced pressure to constant weight (60 mg).

4 (yield 77%). The product exhibits the same spectral characteristics as that prepared from $[PdCl_2(PhCN)_2]$.

4.4. Synthesis of the platinum complex 5

$[PtCl_2(PhCN)_2]$ (48 mg; 0.1 mmol) was added to a cold (5–10°C) solution of **1** (60 mg; 0.1 mmol) in benzene (5 ml). After 1 min stirring, benzene was evaporated. The remaining solid was washed with acetone until it was not longer coloured, and dried under reduced pressure to constant weight (10 mg).

5 (12% yield). Found: C, 54.56; H, 4.40. $C_{39}H_{36}Cl_2O_2P_2Pt$ calc.: C, 54.18; H, 4.20%.

4.5. Synthesis of the platinum complex 6

$[PtCl_2(PhCN)_2]$ (48 mg; 0.1 mmol) was added to a cold (0°C) solution of **1** (60 mg; 0.1 mmol) in acetone (5 ml). After 2 min stirring, the volatiles were evaporated, and the resulting solid was dried under reduced pressure to constant weight (83 mg).

6 (96% yield). Found: C, 54.82; H, 4.69. $C_{39}H_{36}Cl_2O_2P_2Pt$ calc.: C, 54.18; H, 4.20%.

4.6. Synthesis of the platinum complex 7

$[PtCl_2(cod)]$ (38 mg; 0.1 mmol) was added to a cold (0°C) solution of **1** (60 mg; 0.1 mmol) in acetone (5 ml). After 30 min stirring, the volatiles were evaporated and the resulting solid was dried under reduced pressure to constant weight (68 mg).

7 (78% yield). Found: C, 54.33; H, 4.31. $C_{39}H_{36}Cl_2O_2P_2Pt$ calc.: C, 54.18; H, 4.20%.

4.7. Synthesis of the rhodium complex 8

4.7.1. From $[Rh(cod)_2]BF_4$

The diphosphine **1** (370 mg; 0.62 mmol) and $[Rh(cod)_2]BF_4$ (250 mg; 0.62 mmol) were dissolved in a dichloromethane : tetrahydrofuran mixture (15.5 ml) at room temperature. Hexane (6 ml) was then added and the mixture stirred for 1 h. Cooling to 0–5°C for 3 h gave a yellow-orange solid which was filtered, washed with diethyl ether and dried. It was further dissolved in dichloromethane and the resulting solution passed through a pad of celite to give a clear filtrate. Concentration of the filtrate gave an orange solid which was dried under reduced pressure to constant weight (380 mg).

8 (68% yield). Found: C, 62.42; H, 6.00. $C_{47}H_{48}BF_4O_2P_2Rh$ calc.: C, 62.94; H, 5.36%.

4.7.2. From $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$

A solution of $AgBF_4$ (24 mg; 0.124 mmol) in methanol (1 ml) was added to a solution of $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ (30 mg; 0.060 mmol) in dichloromethane (1 ml). After 10 min stirring, a solution of **1** (73 mg; 0.122 mmol) in dichloromethane (2 ml) was added. After 5 min stirring, the AgCl precipitate was filtered and washed with dichloromethane. Evaporation of the solvent gave an orange solid which was washed with diethyl ether and dried under reduced pressure to constant weight (60 mg).

8 (55% yield).

4.8. Synthesis of the rhodium complex 9

A solution of **1** (390 mg; 0.65 mmol) in acetone (5 ml) was added to a solution of [Rh(acac)(cod)] (200 mg;

0.65 mmol) in acetone (5 ml). After 6 h stirring, volatiles were evaporated to give a red solid. Diethyl ether (25 ml) was added and the resulting suspension cooled to −20°C overnight. After filtration, the resulting red solution was evaporated to leave a red solid which was dried under reduced pressure to constant weight (350 mg).

9 (67% yield). Found: C, 65.25; H, 5.57. $C_{44}H_{43}O_4P_2Rh$ calc.: C, 66.00; H, 5.41%.

4.9. Synthesis of the rhodium complex ***10***

A solution of $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ (62 mg; 0.125 mmol) in acetone (8 ml) was added to a solution of **1** (150 mg; 0.250 mmol) in acetone (10 ml) at room temperature. The reaction medium was stirred for 30 min during which time a yellow solid precipitated. After cooling to −20°C for 1 h, the solid was filtered at room temperature and dried under reduced pressure to constant weight (135 mg).

10 (99% yield). Found: C, 57.90; H, 5.37. $C_{55}H_{60}Cl_2O_2P_2Rh_2$ calc.: C, 60.51; H, 5.54%.

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