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The co-crystallization of Ru((*R*)-binap)(η^3-Me-allyl)$_2$ and binap dioxide, and synthesis of Ru($Ph_2P(CH_2)_4PPh_2$)(η^3-Me-allyl)$_2$[1]

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Abstract

The molecular structure of the 2-methylallyl species Ru((*R*)-binap)(η^3-Me-allyl)$_2$ (**3**) was established by X-ray crystallography of a crystal of **3a**, the asymmetric unit of which is composed of half of a molecule of **3** and half of a (*R*)-(+)-2,2′-bis(-diphenylphosphinoyl)-1,1′-binaphthyl(binap dioxide) molecule, co-crystallized with two disordered deuterobenzenes; crystals of **3a** are tetragonal, space group *I*422, with $Z = 8$, $a = 21.344(1)$ Å and $c = 36.453(2)$ Å. The structure was solved by direct methods and refined by full-matrix least-squares procedures to $R = 0.034$ and $R_w = 0.032$ for 3431 reflections with $I \geq 3\sigma(I)$. The 1,4-bis(diphenylphosphino)butane (dppb) analogue (**2**) of **3** was also prepared and characterized by ^{1}H and ^{31}P{^{1}H}-NMR spectroscopy and elemental analysis, and the reactivities of **2** and **3** toward halogen acids are discussed.

Keywords: Ruthenium(II) complexes; Binap; Allyl; X-ray crystal structure

1. Introduction

Ruthenium(II) complexes of the type Ru(P–P)(η^3-allyl)$_2$, where P–P is a chiral diphosphine and η^3-allyl is either η^3-C_3H_5 or η^3-$(CH_2)_2C(CH_3)$, have been studied as catalyst precursors for the asymmetric hydrogenation of a range of unsaturated organics by Genêt et al. [1–4] and by Burk et al. [5]. Among the complexes synthesized was a reported Ru((*R*)-binap)(η^3-Me-allyl)$_2$ (**3**) [1,2], but the complex was not well characterized, and in particular the ^{31}P-NMR data (singlets at δ −15, 27 and 40) reported by Genêt et al. cannot be correct [2], although the same group had reported earlier [1] just one singlet at δ 42.2, which is correct (see Section 3). Our interest in allyl complexes of this type is their utility as starting materials in the preparation of complexes of the type [RuX(P–P)]$_2$(μ-X)$_2$, where X is a halogen [3,4,6,7]. We now report the molecular structure of **3** as determined by X-ray analysis of a crystal containing **3** and the dioxide of binap. The structure is compared with those of the *S*,*S*-chiraphos and *S*,*S*-diop analogues of **3** which have been determined previously by Genêt et al. [2]. Also reported is the synthesis of the 1,4-bis(diphenylphosphino)butane analogue Ru(dppb)(η^3-Me-allyl)$_2$ (**2**) and its utility in the preparation of [RuX(dppb)]$_2$(μ-X)$_2$ species.

2. Experimental

2.1. Materials

Reagent grade solvents (Fisher Scientific) were distilled from CaH_2 (CH_2Cl_2), Na (Et_2O, hexanes, THF and toluene), or Mg/I_2 (MeOH and EtOH) under N_2. 1,5-Cyclooctadiene (cod), 3-chloro-2-methylpropene and 1,4-bis(diphenylphosphino)butane (dppb) were

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[1] Dedicated to Prof. Peter Maitlis on the occasion of his 65th birthday and for 25 years of close friendship.

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used as supplied by Aldrich. Mg turnings, anhydrous $MgSO_4$ and neutral alumina were used as supplied by Fisher. Dr Steven King (formerly of Merck) kindly donated the binap. Ruthenium was obtained as $RuCl_3 \cdot xH_2O$ on loan from Johnson Matthey (41.4–44%) or Colonial Metals (39.1%). Manipulations were carried out under Ar using standard Schlenk techniques.

$[RuCl_2(cod)]_x$ was prepared analytically pure by published procedures [2,8], that of Genêt et al. giving a better yield in a shorter reaction time.

2.2. Instrumentation

Solution NMR spectra were recorded on a Bruker AC 200F (81.0 MHz for $^{31}P\{^1H\}$) or a Varian XL300 spectrometer (121.42 MHz for $^{31}P\{^1H\}$), using residual solvent proton (^1H) or external $P(OMe)_3$ ($^{31}P\{^1H\}$: δ 141.00 versus external 85% aq. H_3PO_4) as the reference; ^{31}P chemical shifts are reported with respect to external 85% aq. H_3PO_4. Elemental analyses were performed by P. Borda of this department.

2.3. (η^4-1,5-cyclooctadiene)bis(η^3-2-methylallyl)ruthenium(II), Ru(cod)(η^3-Me-allyl)$_2$ (**1**)

This material was prepared using minor modifications to a literature procedure [2]. 2-Methylallylmagnesium chloride was found to be poorly soluble in Et_2O and therefore THF was used as the solvent. The Grignard reagent (2 M, 6 ml, 12 mmol; prepared from Mg and 3-chloro-2-methylpropene in THF) was added to a suspension of $[RuCl_2(cod)]_x$ (0.28 g, 1.0 mmol Ru) in Et_2O (10 ml)/THF (15 ml) and the mixture stirred at $\sim$20°C for 10 min. The excess Grignard reagent was precipitated from solution by adding Et_2O and the suspension was filtered through Celite. The filtrate was hydrolyzed in ice-water and the mixture extracted with Et_2O (2×20 ml). The organic layer was dried over $MgSO_4$, concentrated, filtered through a short column of neutral alumina (5×5 cm) and evaporated to dryness. Reprecipitation from a mixture of MeOH and petroleum ether gave pure **1**. Yield: 0.27 g (80%). Anal. Calc. for $C_{16}H_{26}Ru$: C, 60.16; H, 8.20. Found: C, 59.93; H, 8.31%. m.p. = 80–85°C. ^1H-NMR (300 MHz, C_6D_6, 20°C): δ 0.20 (s, 2H, *anti*-H of Me-allyl), 1.08–1.26 (m, 2H, C*H* of cod), 1.45–1.70 (m, 4H, CH_2 of cod), 1.56 (s, 2H, *syn*-H of Me-allyl), 1.70 (s, 6H, CH_3 of Me-allyl), 2.64–3.00 (m, 4H, CH_2 of cod), 2.88 (s, 2H, *anti*-H of Me-allyl), 3.52 (d, 2H, $J = 2$ Hz, *syn*-H of Me-allyl), 3.98 (dd, 2H, $J = 5$, 9 Hz, C*H*– of cod). $^{13}C\{^1H\}$-NMR (C_6D_6, 20°C): δ 24.74 (*C*H_3 of Me-allyl), 26.26 and 38.34 ($CH_3C(CH_2)_2$), 51.22 and 51.68 (*C*H_2 of cod), 70.63 and 88.22 (*C*H– of cod), 111.49 ($CH_3C(CH_2)_2$). The physical [9] and ^1H-NMR [10] data agree with those reported in the literature, while the $^{13}C\{^1H\}$-NMR data have not been reported previously.

2.4. (1,4-bis(diphenylphosphino)butane)bis(η^3-2-methylallyl)ruthenium(II), Ru(dppb)(η^3-Me-allyl)$_2$ (**2**)

Complex **2** was prepared from **1** using a modified literature procedure [2]. One equivalent of dppb (0.13 g, 0.31 mmol) and **1** (0.10 g, 0.31 mmol) were dissolved in CH_2Cl_2 (1 ml) and heated in a Schlenk tube to 40°C under a flow of Ar. The colorless solution slowly became yellow. After the reaction mixture was heated for 18 h, the solvent was removed under vacuum. The yellow solid was transferred onto a filter, washed with hexanes (4×2 ml) and Et_2O (2×2 ml), and dried under vacuum. Yield: 0.15 g (76%). Anal. Calc. for $C_{36}H_{42}P_2Ru$: C, 67.80; H, 6.64. Found: C, 67.52; H, 6.64%. ^1H-NMR (300 MHz, C_6D_6, 20°C): δ 1.09 (center of unresolved AB quartet, 2H, C*H* of Me-allyl), 1.43 (s, 2H, C*H* of Me-allyl), 1.49 (s, 2H, C*H* of Me-allyl), 1.55 (br m, 2H, CH_2 of dppb), 1.70 (br m, 2H, CH_2 of dppb), 2.10 (s, 6H, CH_3 of Me-allyl), 2.19 (br m, 2H, CH_2 of dppb), 2.52 (s, 2H, C*H* of Me-allyl), 2.59 (br m, 2H, CH_2 of dppb), 6.85–7.37 (m, 16H, *o*-, *m*-H), 7.86 (t, 4H, $J = 8.8$ Hz, *p*-H). $^{31}P\{^1H\}$-NMR (121.42 MHz, C_6D_6, 20°C): 44.2, s; ($CDCl_3$, 20°C): 44.1, s.

2.5. ((R)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl)bis(η^3-2-methylallyl)ruthenium(II), Ru((R)-binap)(η^3-Me-allyl)$_2$ (**3**)

Complex **3** was synthesized by modifying a procedure of Genêt et al. [2]. One equivalent of (*R*)-binap (0.15 g, 0.24 mmol) and **1** (0.078 g, 0.24 mmol) were refluxed in toluene (2 ml) for 4 h under Ar. The resulting orange/brown solution was reduced to dryness, and the dark-orange residue was placed on a filter and washed with hexanes (4×2 ml). The orange washings were reduced to dryness at the pump, while the brown solid remaining on the filter was dried under vacuum ($\sim$90 mg). $^{31}P\{^1H\}$-NMR (121.42 MHz, C_6D_6, 20°C) of the orange residue ($\sim$60 mg): singlets at $\delta = 42.1$ (**3**) and -15.0 (free binap). $^{31}P\{^1H\}$-NMR (121.42 MHz, C_6D_6, 20°C) of the brown solid: singlets at $\delta = 42.1$ (**3**), -15.0 (free binap) and 26.6 (binap$(O)_2$). An orange crystal suitable for X-ray diffraction studies was deposited over several weeks from a C_6D_6 solution stored in a stoppered NMR tube, the solution showing singlets for **3**, binap and binap$(O)_2$ in the $^{31}P\{^1H\}$-NMR spectrum; the solution had changed from orange to dark green in color. The X-ray diffraction data showed the asymmetric unit of the crystal (**3a**) to be composed of half a molecule of **3** and half of a (*R*)-(+)-2,2′-bis(diphenylphosphinoyl)-1,1′-binaphthyl ((*R*)-binap$(O)_2$) molecule, co-crystallized with two disordered deuterobenzenes (see Sections 2.6 and 3). The 'three singlets' $^{31}P\{^1H\}$-NMR data are in agreement with those previously reported but without assignments [2]. The ^1H-NMR data were essentially the same as those described by Genêt et al.

2.6. X-ray crystallographic analysis of **3a**

Crystallographic data for **3a** appear in Table 1. The final unit-cell parameters were obtained by full-matrix least-squares on the setting angles for 25 reflections in the range $66.6 < 2\theta < 82.9°$.

The structure was solved by direct methods and expanded using Fourier techniques. The asymmetric unit of **3a** consists of half a Ru((*R*)-binap)(η^3-Me-allyl)$_2$ molecule, half a binap(O)$_2$ and two disordered deuterobenzene regions, while the unit cell contains eight molecules each of the ruthenium and binap dioxide moieties. One of the C_6D_6 molecules is (1:1) disordered about a 2-fold axis, the population parameters for this moiety (C(49–54) were fixed at 0.50). The second solvent is disordered about a 4-fold axis. The electron density in this region was modeled by refining the four peaks in this region as C-atoms and the site occupancy parameters for these atoms were refined. This treatment adequately accounted for the electron density in the region. The geometrical parameters for the solvent molecules deviate from the expected values and are therefore excluded from the tables (Section 5). The benzene C-atoms were refined isotropically, while the remaining non-hydrogen atoms were refined anisotropically. All H-atoms except those associated with the benzene molecule located near the 4-fold axis were fixed in calculated positions with C–H = 0.98 Å.

A parallel refinement of the opposite enantiomorph (see Section 3) resulted in substantially higher residuals, the *R* and R_w factor ratios being 1.36 and 1.33, respectively. All calculations were performed using the teXsan crystallographic software package [11]. Neutral atom scattering factors and anomalous dispersion corrections for all atoms were taken from ref. [12]. Selected bond lengths and angles appear in Table 2. See also Section 5.

Table 1
Crystallographic data

Compound	**3a**[a]
Formula	$C_{105.52}H_{87.52}O_2P_4Ru$
Formula weight	1612.58
Color, habit	Orange, prism
Crystal size (mm)	$0.25 \times 0.35 \times 0.35$
Crystal system	Tetragonal
Space group	*I*422
a (Å)	21.344(1)
c (Å)	36.453(2)
V	16606.0(9)
Z	8
T (°C)	21
Calculated density (g cm^{-3})	1.290
F(000)	6725.12
Radiation	Cu
μ (cm^{-1})	26.61
Transmission factors	0.639–1.000
Scan type	$\omega-2\theta$
Scan range (° in ω)	$0.94+0.20 \tan\theta$
Scan speed (° min^{-1})	32 (up to nine scans)
Data collected	$+h, +k, +l$ ($k<l$)
$2\theta_{max}$ (°)	155
Crystal decay (%)	Negligible
Total no. of reflections	4918
Unique reflections	4918
No. with $I \geq 3\sigma(I)$	3431
No. of variables	510
R	0.034
R_w	0.032
GOF	1.85
Max Δ/σ (final cycle)	0.02
Residual density (e Å^{-3})	−0.29, 0.27

[a] Rigaku AFC6S diffractometer, take-off angle 6.0, aperture 6.0×6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1), Cu K_α radiation ($\lambda = 1.54178$ Å), graphite monochromator, $w = 4F_o^2/\sigma^2(F_o^2)$. $\sigma^2(F^2) = [S^2(C+4B)^2]/Lp^2$ (*S*, scan speed; *C*, scan count and *B*, normalized background count), function minimized $\Sigma w(|F_o|-|F_c|)^2$, $R = S||F_o|-|F_c||/S|F_o|$, $R_w = (\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, and GOF $= [\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$. Values given for *R*, *Rw* and GOF are based on those reflections with $I \geq 3\sigma(I)$.

Table 2
Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

	3a		
Ru(1)–P(1)	2.339(1)	Ru(1)–C(23)	2.228(4)
Ru(1)–C(24)	2.178(5)	Ru(1)–C(25)	2.240(5)
Ru(1)–A[a]	1.96	P(1)–C(1)	1.845(5)
P(1)–C(11)	1.857(5)	P(1)–C(17)	1.844(5)
P(2)–O(1)	1.478(4)	P(2)–C(27)	1.795(6)
P(2)–C(37)	1.811(6)	P(2)–C(43)	1.807(6)
C(23)–C(24)	1.403(7)	C(24)–C(25)	1.388(8)
C(24)–C(26)	1.529(8)	C(28)–C(28)″	1.504(10)
C(27)–C(28)	1.380(7)		
P(1)–Ru(1)–P(1)′	91.92(6)	P(1)–Ru(1)–C(23)	86.8(2)
P(1)–Ru(1)–C(23)′	97.1(1)	P(1)–Ru(1)–C(24)	119.2(2)
P(1)–Ru(1)–C(24)′	111.4(2)	P(1)–Ru(1)–C(25)	152.2(2)
P(1)–Ru(1)–C(25)′	89.1(2)	P(1)–Ru(1)–A	119.8
P(1)–Ru(1)–A′	100.2	C(23)–Ru(1)–C(23)′	174.4(3)
C(23)–Ru(1)–C(24)	37.1(2)	C(23)–Ru(1)–C(24)′	137.6(2)
C(23)–Ru(1)–C(25)	65.6(2)	C(23)–Ru(1)–C(25)′	110.7(2)
C(24)–Ru(1)–C(24)′	104.4(3)	C(24)–Ru(1)–C(25)	36.6(2)
C(24)–Ru(1)–C(25)′	92.1(2)	C(25)–Ru(1)–C(25)′	102.7(3)
A–Ru–A′	122.0	Ru(1)–P(1)–C(1)	109.3(1)
Ru(1)–P(1)–C(11)	116.8(2)	Ru(1)–P(1)–C(17)	128.1(2)
C(1)–P(1)–C(11)	100.8(2)	C(1)–P(1)–C(17)	103.7(2)
C(11)–P(1)–C(17)	94.3(2)	O(1)–P(2)–C(27)	117.1(3)
O(1)–P(2)–C(37)	111.4(3)	O(1)–P(2)–C(43)	110.6(3)
C(27)–P(2)–C(37)	104.9(3)	C(27)–P(2)–C(43)	106.0(3)
C(37)–P(2)–C(43)	106.1(3)	P(1)–C(1)–C(2)	123.9(4)
P(1)–C(1)–C(10)	117.5(4)	P(1)–C(11)–C(12)	121.6(4)
P(1)–C(11)–C(16)	121.1(4)	P(1)–C(17)–C(18)	123.1(4)
P(1)–C(17)–C(22)	118.7(4)	P(2)–C(27)–C(28)	122.8(4)
P(2)–C(27)–C(36)	120.0(5)	C(27)–C(28)–C(28)″	119.8(5)
P(2)–C(37)–C(38)	117.2(5)	P(2)–C(37)–C(42)	123.5(5)
P(2)–C(43)–C(44)	117.4(5)	P(2)–C(43)–C(48)	124.3(6)

[a] A and A′ refer to the unweighted centroid of the three coordinated carbon atoms of the methylallyl ligand. Symmetry operations: (′) *y*, *x*, $1-z$; (″) $1/2-y$, $1/2-x$, $1/2-z$.

3. Results and discussion

3.1. Ru(P–P)(η^3-Me-allyl) complexes; **1** (P–P = (R)-binap) and **2** (P–P = dppb)

The reported routes by Genêt and co-workers to a variety of Ru(P–P)(η^3-allyl)$_2$ complexes, where P–P = chiral phosphine and allyl = allyl or Me-allyl, have involved refluxing a 1:1 mixture of the diphosphine and Ru(cod)(allyl)$_2$ complex in hexanes or toluene [1,2,13]. Our excursion into the use of π-allyl complexes as precursors resulted from an interest in finding alternative routes to [RuX(dppb)]$_2$(μ-X)$_2$ complexes (X = halogen), the chloro species and its diverse chemistry having been studied extensively in this laboratory [6,7,14–17]. The preparation of the Ru(dppb)(η^3-Me-allyl)$_2$ (**2**) was thus undertaken, as Genêt and co-workers had shown that isolated Ru(P–P)(allyl)$_2$ species react with HCl and HBr to give in situ the required $Ru_2X_4(P–P)_2$ complexes [3,4]. An attempt to follow the preparative method (using refluxing hexanes [1,2]) was not effective for the preparation of **2**, which like the binap analogue **3** also contains a seven-membered chelate (P–P) ring; however, if the Ru(cod)(η^3-Me-allyl)$_2$ and dppb were refluxed in CH_2Cl_2, pure **2** was readily isolated, the C_6D_6 $^{31}P\{^1H\}$ solution spectrum showing a singlet at δ 44.2 (Section 2.4). We had initially attempted the preparation of **3** using the same procedure but only the starting materials were isolated on work-up from the CH_2Cl_2 solution; the reaction was thus subsequently performed in refluxing toluene (see Section 2.5).

The synthesis of Ru((*R*)–binap)(η^3-Me-allyl)$_2$ (**3**) has been reported by Genêt and co-workers [1,2]; however, no micro-analytical data were given and the $^{31}P\{^1H\}$-NMR data (singlets at δ 40, 27 and −15 [2]) were not discussed. In the present work, difficulty was encountered in isolating **3** free of trace binap. The three ^{31}P singlets are now assigned confidently to **3**, (*R*)-binap(O)$_2$ and free binap, respectively. An authentic sample of binap(O)$_2$ was prepared in situ by the H_2O_2-oxidation of binap in C_6D_6, and addition of the oxide to a solution of the brown material isolated in the preparation of **3** in C_6D_6 increased the intensity of the δ 26.6 resonance. X-ray analysis of the crystal **3a** reveals that complex **3** co-crystallizes with (*R*)-binap dioxide.

The molecular structure of **3** (Fig. 1) shows the complex to be chiral at the metal center (Λ, assuming an octahedral-type coordination), and therefore one of the two possible diastereomers has crystallized (i.e. Λ, *R*; where the first designation is the metal center and the second is the chirality of the diphosphine). The molecule possesses C_2 symmetry (Fig. 1). The geometry around the Ru can be described as either strongly distorted tetrahedral or strongly distorted octahedral, the tetrahedron being defined by the two P-atoms and the two central carbons of the planar η^3-Me-allyl ligands, and the octahedron being defined by the two P-atoms and the four methylene carbons of the two 2-methylallyl ligands. Distortions from tetrahedral are caused by the rigid chelating binap ligand (i.e. the P(1)–Ru–P(1)′ angle is 91.9°). Distortions from octahedral are also evident (e.g. the C(23)–Ru–C(25) angle is 65.6°) and are the result of the requirement that the 2-methylallyl ligand be planar. The fact that the central carbons of the 2-methylallyl ligands are closer to the Ru than the end allyl carbons (Ru(1)–C(24) 2.178 Å compared with Ru(1)–C(23) 2.228 Å and Ru(1)–C(25) 2.240 Å) favors viewing the coordination sphere as a tetrahedron.

An X-ray diffraction study of Ru(PPh$_3$)$_2$(η^3-allyl)$_2$ showed the Ru to be tetrahedrally coordinated, the P–Ru–P bond angle being 109.9° and the P–Ru–C (central carbon of allyl) bond angles ranging from 108.8–112.4° [18]. The Ru–P bond distance of 2.342 Å is identical (within experimental error) to that observed in **3**, while the central carbons of the allyl ligands are again comparably closer to the Ru than the end allyl carbons.

The structures of the Ru(P–P)(η^3-Me-allyl)$_2$ complexes, where P–P = (*S*,*S*)-diop or (*S*,*S*)-chiraphos, have been described as distorted octahedral [2], but are in fact similar to the molecular structure of **3**. For example, the P–Ru–P bond angles are 96.8 (diop) and 84.96° (chiraphos), again significantly smaller than the 109.9° seen for the monodentate PPh$_3$ analogue.

On coordination of (*R*)-binap to Ru a seven-membered chelate ring is formed, the conformation of

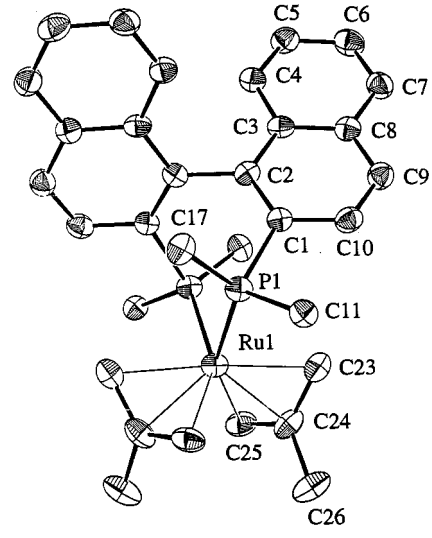

Fig. 1. The ORTEP plot of Ru((*R*)-binap)(η^3-Me-allyl)$_2$ **3**. Thermal ellipsoids for non-hydrogen atoms are drawn at 33% probability (some of the phenyl carbons have been omitted for clarity). A C_2 axis rotates the labeled half of the molecule into the non-labeled half (e.g. P(1) reflects into P(1)′).

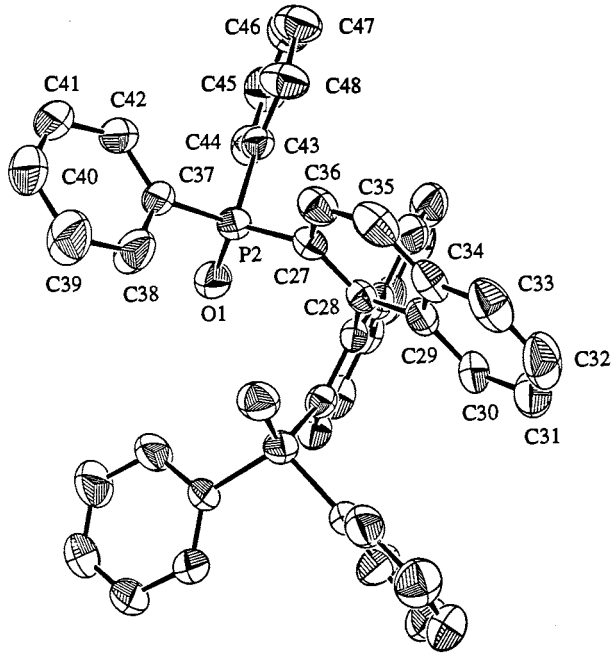

Fig. 2. The ORTEP plot of (*R*)-(+)-2,2′-bis(diphenylphosphinoyl)-1,1′-binaphthyl (binap(O)$_2$). Thermal ellipsoids for non-hydrogen atoms are drawn at 33% probability (some of the phenyl carbons have been omitted for clarity). A C_2 axis rotates the labeled half of the molecule into the non-labeled half (e.g. P(2) reflects into P(2)′).

which, in the case of **3**, and more generally [19], is λ. The angle between the least-squares planes of the two naphthyl rings in **3** is 68.2°.

The other molecule present in the crystal of **3a** is (*R*)-binap(O)$_2$ (Fig. 2) which also possesses C_2 symmetry. An X-ray diffraction study has previously been performed on a 1:1:1:1 complex of (S)-binap(O)$_2$, (1*R*)-camphorsulfonic acid, acetic acid and ethyl acetate [20], but the molecular structures of (*R*)-binap(O)$_2$ determined here, and that determined by Takaya et al. are significantly different, probably because of the H-bonding interactions between the phosphine oxide and the camphorsulfonic and acetic acid groups, and the different space groups (*P*1 and, in the present work, *I*422). The P–O bond length of 1.478 Å observed here compares with those of 1.506 and 1.483 Å observed by Takaya et al., but the angle between the least-squares planes of the naphthyl rings, which in **3a** was 79.3°, was 90.3° in the quaternary complex [20]. There are no H-bonding interactions between **3** and binap(O)$_2$ in the **3a** structure.

3.2. *[RuX(dppb)]$_2$(μ-X)$_2$ complexes (X = halogen); X = Cl (**4**)*

Reaction of Ru(dppb)(η^3-Me-allyl)$_2$ (**2**) in $CDCl_3$ with two equivalents of aq. HX (in MeOH) produced in situ the corresponding [RuX(dppb)]$_2$(μ-X)$_2$ complexes, X = Cl, Br, and I (Eq. (1)). This was demonstrated by $^{31}P\{^1H\}$-NMR spectroscopy, as the δ 44.2 singlet of **2** decreased in intensity on addition of HX, while the AB pattern corresponding to the appropriate dimer [6,7,14–17] became apparent (Fig. 3). It should be noted that we have recently shown that '[RuCl(dppb)]$_2$(μ-Cl)$_2$' is actually isolated as [RuCl(dppb)]$_2$(μ-Cl)$_2$(μ-H_2O), although in solution the bridging H_2O readily dissociates from the complex [17].

$$2\text{Ru(dppb)}(\eta^3\text{-Me-allyl})_2 + 4\text{HX} \rightarrow [\text{RuX(dppb)}]_2(\mu\text{-X})_2 + 4\text{Me}_2\text{C=CH}_2 \quad (1)$$

The broad resonance at δ_P 57 (Fig. 3) results from interaction of MeOH with the in situ [RuCl$_2$(dppb)]$_2$(μ-Cl)$_2$ product, but the nature of the complex formed remains uncertain. This resonance also results from interaction of excess MeOH with a $CDCl_3$ solution of isolated [RuCl$_2$(dppb)]$_2$(μ-Cl)$_2$(μ-H_2O) and so cannot arise from a 2-methylpropene derived species (cf. Eq. (1)). From a consideration of the reactants and the solvent used (which sometimes contains traces of HCl), plausible products, which are all known species, include: the anionic species (**5**) [17,21] formed via trace chloride present (Eq. (2)), the mixed-valence compound (**6**) [6,7,22] formed via trace HCl present (see the reverse of Eq. (3), the forward reaction of which is known

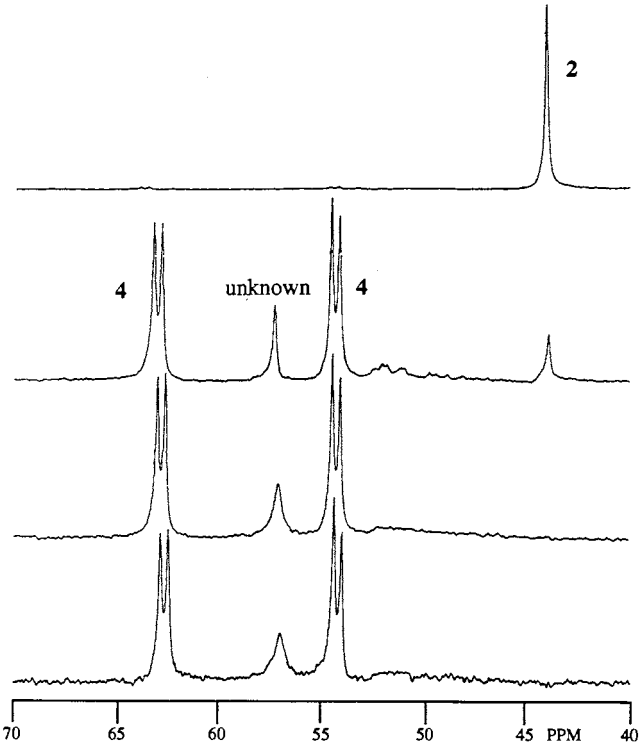

Fig. 3. $^{31}P\{^1H\}$-NMR spectra (121.42 MHz, 20°C) of Ru(dppb)(η^3-Me-allyl)$_2$ **2** in $CDCl_3$ with: (a) no added HCl, (b) one equivalent HCl, (c) two equivalents HCl, and (d) three equivalents HCl. [RuCl(dppb)]$_2$(μ-Cl)$_2$, **4**. δ_A 63.5, δ_B 54.3 (J_{AB} 46.9 Hz). For the dimeric bromo and iodo species the corresponding data are δ_A 65.2, δ_B 55.6 (J_{AB} 44.3 Hz) and δ_A 70.1, δ_B 55.6 (J_{AB} 39.9 Hz), respectively [17].

[6]), or $[Ru_3Cl_5(dppb)_3]Cl$ (**7**), as the corresponding binap [23] and 1,2-bis(diphenylphosphino)benzene [24] analogues have been made by refluxing [RuCl(arene)(P–P)]Cl precursors in MeOH.

$$[RuCl(dppb)]_2(\mu\text{-}Cl)_2\ (\mathbf{4}) + Cl^- \rightarrow \{[RuCl(dppb)]_2(\mu\text{-}Cl)_3\}^-\ (\mathbf{5}) \quad (2)$$

$$[RuCl(dppb)]_2(\mu\text{-}Cl)_3\ (\mathbf{6}) + 1/2H_2 \rightleftharpoons [RuCl(dppb)]_2(\mu\text{-}Cl)_2\ (\mathbf{4}) + HCl \quad (3)$$

However, **5** shows a δ_P singlet at 49 and **6** is NMR-inactive, while the binap analogue of **7** gives a δ_P singlet at 49.7 in $CDCl_3$ [23]. Thus, **7** appears the most likely species giving the δ_P 57 resonance. However, it should be noted also that $RuCl_3(dppb)(H_2O)$ (**8**) has been isolated as red crystals from a reaction between aq. HCl (in MeOH) and $[RuCl(dppb)]_2(\mu\text{-}Cl)_2$ in $CDCl_3$ and its formulation established by X-ray analysis [25]; unfortunately the isolated **8** is insufficiently soluble in $CDCl_3$, C_6D_6 or other common non-coordinating solvents to confirm its possible association with the δ_P 57 singlet. Even the possibility of the formation of the η^1-HCl adduct $(HCl)(dppb)Ru(\mu\text{-}Cl)_3RuCl(dppb)$ cannot be completely ruled out as the corresponding MeI adduct has been identified ([7] and see below) and such HCl adducts have been formulated within Pt(II) systems [26]. Also plausible are species with coordinated MeOH.

$[RuI(dppb)]_2(\mu\text{-}I)_2$ species produced in situ by addition of two equivalents of HI to **2** has been shown to be an effective catalyst for imine hydrogenation [17].

Of interest, addition of $NEt_3 \cdot HCl$ to $Ru(dppb)(\eta^3\text{-Me-allyl})_2$ (**2**) in $CDCl_3$ gave a resonance at δ 48.9 attributed to $Ru_2Cl_4(dppb)_2(NEt_3)$ [7,27], the binap analogue of which is a very effective asymmetric homogeneous hydrogenation catalyst [28]. The chemistry presumably follows Eq. (1) with subsequent addition of NEt_3 to $[RuCl(dppb)]_2(\mu\text{-}Cl)_2$ [7].

Attempts to prepare $[RuCl((R)\text{-binap})]_2(\mu\text{-}Cl)_2$ by addition of aq. HCl (in MeOH) to the isolated solid containing $Ru((R)\text{-binap})(\eta^3\text{-Me-allyl})_2$ and $binap(O)_2$ gave an in situ $^{31}P\{^1H\}$-NMR spectrum in C_6D_6 which did not include resonances corresponding to those of $[RuCl(binap)]_2(\mu\text{-}Cl)_2$ [7]. The spectrum showed numerous overlapping resonances between δ 50–70, which are probably AB quartets, but these are impossible to assign because of the complexity of the spectrum; the resonance at δ 42.1 for the reactant Me-allyl complex **3** is completely eliminated on addition of HCl. Genêt et al. have assumed that $[RuCl(binap)]_2(\mu\text{-}Cl)_2$ species or solvated derivatives are formed cleanly from such a protonation reaction in a range of solvents [2–4], but the chemistry is undoubtedly more complex; other possible products include binap analogues of **5–7** and species of the type $L(binap)Ru(\mu\text{-}Cl)_3RuCl(binap)$ which are well documented in the case of the dppb analogues where L is, for example, η^2-H_2, N_2, acetone, DMSO, PhCN or MeI [7].

4. Conclusions

The molecular structure of $Ru((R)\text{-binap})(\eta^3\text{-Me-allyl})_2$ (**3**) is established by X-ray diffraction on a crystal which contains a molecule of **3** and a molecule of $binap(O)_2$, co-crystallized with disordered deuterobenzenes. The $Ru(dppb)(\eta^3\text{-Me-allyl})_2$ complex (**2**) is synthesized and its utility as a starting material for the complexes $[RuX(dppb)]_2(\mu\text{-}X)_2$ is shown (X = halogen).

5. Supplementary material

Tables of atomic coordinates and equivalent isotropic thermal parameters, hydrogen atom parameters, anisotropic thermal parameters, complete lists of bond lengths and angles, torsion angles, intermolecular contacts, least-squares planes, and measured and calculated structure factor amplitudes for **3a** are available on request from the authors.

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References

[1] J.P. Genêt, S. Mallart, C. Pinel, S. Juge, J.A. Laffitte, Tetrahedron: Asymmetry 2 (1991) 43.
[2] J.P. Genêt, C. Pinel, V. Ratovelomanana-Vidal, S. Mallart, X. Pfister, M.C. Caño De Andrade, J.A. Laffitte, Tetrahedron: Asymmetry 5 (1994) 665.
[3] J.P. Genêt, C. Pinel, S. Mallart, S. Juge, S. Thorimbert, J.A. Laffitte, Tetrahedron: Asymmetry 2 (1991) 555.
[4] J.P. Genêt, C. Pinel, V. Ratovelomanana-Vidal, et al., Tetrahedron: Asymmetry 5 (1994) 675.
[5] M.J. Burk, T.G.P. Harper, C.S. Kalberg, J. Am. Chem. Soc. 117 (1995) 4423.
[6] B.R. James, A. Pacheco, S.J. Rettig, I.S. Thorburn, R.G. Ball, J.A. Ibers, J. Mol. Catal. 41 (1987) 147.
[7] A.M. Joshi, I.S. Thorburn, S.J. Rettig, B.R. James, Inorg. Chim. Acta 198–200 (1992) 283.
[8] M.A. Bennett, G. Wilkinson, Chem. Ind. (London) (1959) 1516.
[9] J. Powell, B.L. Shaw, J. Chem. Soc. (A) (1968) 160.
[10] R.R. Schrock, B.F.G. Johnson, J. Lewis, J. Chem. Soc. Dalton Trans. (1974) 951.
[11] teXsan: Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, USA, 1985 and 1992.

[12] (a) D.C. Creagh, W.J. McAuley, in: A.J.C. Wilson (Ed.), International Tables for Crystallography, vol. C, Kluwer Academic, Boston, USA, 1992, pp. 219–222. (b) D.C. Creagh, J.H. Hubbell, in: A.J.C. Wilson (Ed.), International Tables for Crystallography, vol. C, Kluwer Academic, Boston, USA, 1992, pp. 200–206.
[13] J.P. Genêt, C. Pinel, S. Mallart, S. Juge, N. Cailhol, J.A. Laffitte, Tetrahedron Lett. 33 (1992) 5343.
[14] A.M. Joshi, B.R. James, J. Chem. Soc. Chem. Commun. (1989) 1785.
[15] D.E.K.-Y. Chau, B.R. James, Inorg. Chim. Acta 240 (1995) 419.
[16] A.M. Joshi, K.S. MacFarlane, B.R. James, J. Organometal. Chem. 488 (1995) 161.
[17] K.S. MacFarlane, I.S. Thorburn, P.W. Cyr, D.E.K.-Y. Chau, S.J. Rettig, B.R. James, Inorg. Chim. Acta, in press.
[18] A.E. Smith, Inorg. Chem. 11 (1972) 2306.
[19] R. Noyori, Chemtech (1992) 360.
[20] H. Takaya, K. Mashima, K. Koyano, et al., J. Org. Chem. 51 (1986) 629.
[21] S.N. Gamage, R.H. Morris, S.J. Rettig, D.C. Thackray, I.S. Thorburn, B.R. James, J. Chem. Soc. Chem. Comm. (1987) 894.
[22] I.S. Thorburn, S.J. Rettig, B.R. James, Inorg. Chem. 25 (1986) 234.
[23] (a) K. Mashima, T. Hino, H. Takaya, Tetrahedron Lett. 32 (1991) 3101. (b) K. Mashima, T. Hino, H. Takaya, J. Chem. Soc. Chem. Commun. (1992) 2099.
[24] K. Mashima, N. Komura, T. Yamagota, K. Tani, M. Haga, Inorg. Chem. 36 (1997) 2908.
[25] A.A. Batista, K.S. MacFarlane, B.R. James, to be published.
[26] R. Kuhlman, H. Rothfuss, D. Gusev, W.E. Streib, K.G. Caulton, 209th Am. Chem. Soc. National Meeting, Anaheim, CA, 1995, Abstract INORG 497.
[27] D.E. Fogg, B.R. James, Inorg. Chem. 34 (1995) 2557.
[28] R. Noyori, Asymmetric Catalysis in Organic Synthesis, Wiley-Interscience, New York, 1994, Chapter 2.