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Note

Synthesis, characterization, and catalytic behaviour of a dimeric ruthenium(II) methoxydiphenylphosphane complex

Eric Dulière [a], Bernard Tinant [b], André Schanck [b], Michel Devillers [c], Jacqueline Marchand-Brynaert [a,*]

[a] *Laboratoire de Chimie Organique de Synthèse, Département de Chimie, Université Catholique de Louvain, Bâtiment Lavoisier, Place Louis Pasteur, 1, B-1348 Louvain-la-Neuve, Belgium*

[b] *Laboratoire de Chimie Physique et Cristallographie, Département de Chimie, Université Catholique de Louvain, Bâtiment Lavoisier, Place Louis Pasteur, 1, B-1348 Louvain-la-Neuve, Belgium*

[c] *Laboratoire de Chimie Inorganique et Analytique, Département de Chimie, Université Catholique de Louvain, Bâtiment Lavoisier, Place Louis Pasteur, 1, B-1348 Louvain-la-Neuve, Belgium*

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Abstract

Reaction of dichlorotetrakis(dmso)ruthenium(II) with methoxydiphenylphosphane in refluxing methanol gave dichlorotris-(methoxydiphenylphosphane)ruthenium(II) which dimerizes. The structure of the dimer was established by NMR and X-ray diffraction analyses; this ruthenium complex catalyzed the oxidation of alcohols by *N*-methylmorpholine oxide.

Keywords: Ruthenium complexes; Methoxydiphenylphosphane; Crystal structures; Catalytic oxidation

1. Introduction

The need for practical recovery of transition metal catalysts from homogeneous organic media [1] has led to the development of new catalytic systems combining the advantages of heterogeneous and homogeneous catalysts. The principle of *heterogenization of homogeneous catalysis* consists in the attachment of a homogeneous catalyst onto an insoluble organic polymer, or silica support, in such a manner that the catalyst operates as if it were in solution [2]. Immobilization of transition metal complexes has been particularly well illustrated in the case of rhodium complexes useful in various organic reduction processes [3]; the catalysts could be recycled and reused without significant loss of activity, or selectivity. Ruthenium catalysts were similarly anchored on solid supports and used in hydrogenation [4] and hydrogen transfer reactions [5]. On the other hand, oxidation reactions catalyzed by polymer-supported ruthenium catalysts appeared to be scarcely described in the literature [6]. This most probably results from the high sensitivity of the usual phosphine ligands towards oxidation; consequently, the recovery and reuse of such catalysts could not be a realistic objective.

During the search of new ruthenium ligands susceptible to fulfil the conditions for immobilization of oxidation catalysts onto solid supports, we considered the phosphinite derivatives. This class of ligands has been recently developed in the field of the enantioselective hydrogenation catalyzed by optically-active complexes of rhodium [7] and ruthenium [8]. To our knowledge, oxidation catalysts based on ruthenium surrounded with phosphinite ligands have not been described yet. We report here the synthesis, spectroscopic and crystallographic characterization, as well as the catalytic behaviour of a complex made of Ru(II) and methoxydiphenylphosphane as stable ligand.

* Corresponding author. Tel.: +32-10-472 746; fax: +32-10-474 168.

E-mail address: marchand@chor.ucl.ac.be (J. Marchand-Brynaert).

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2. Experimental

2.1. Measurements

Elemental analyses (C, H, P) were carried out at University College London, Chemistry Department, Christopher Ingold Laboratories. Proton (200 MHz) and carbon (50 MHz) NMR spectra were recorded on a Varian Gemini 200 NMR spectrometer with $CDCl_3$ as the solvent and $SiMe_4$ as the internal reference. The $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$ solution on a Bruker WM250 spectometer at 250 MHz with H_3PO_4 as an external reference.

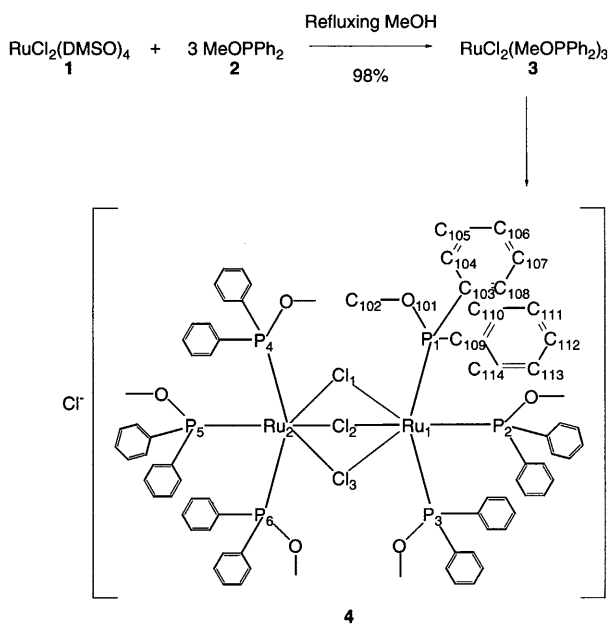
2.2. Materials

Reagents were purchased from Acros and used without further purification. Solvents were of analytical purity. Dichloromethane and dimethylsulfoxide were used as received. Methanol was dried over magnesium turnings and distilled prior to use.

2.3. Preparations

Dichlorotetrakis(dimethylsulfoxide)ruthenium was prepared as described in the literature [9].

Dichlorotetrakis(dimethylsulfoxide)ruthenium (0.092 g, 0.19 mmol) was dissolved in methanol (10 cm^3) and refluxed for ten minutes. Methoxydiphenylphosphane (0.14 cm^3, 0.70 mmol) was then added and the dark red resulting solution was refluxed further for 30 min. The mixture was concentrated to an oil and precipitated by addition of diethylether (5 cm^3). The product was purified by gel permeation in a home-made glass column packed with LH20 Sephadex gel and eluted by methanol to yield 0.16 g (0.19 mmol) of $RuCl_2(MeOPPh_2)_3 \cdot H_2O$. (decomp. 197–199°C). *Anal.* Found: C, 55.60; H, 4.91; P, 10.69. Calc. for $C_{39}H_{39}Cl_2O_3P_3Ru \cdot H_2O$: C, 55.86; H, 5.06; P, 11.08%. The presence of water molecule in the complex has been confirmed by thermogravimetry. A single crystal for X-ray analysis was obtained by slow evaporation from methanol solution.



Scheme 1.

2.4. X-ray analysis

Crystal data for $[\{Ru(MeOPPh_2)_3\}_2(\mu_2\text{-}Cl)_3]Cl \cdot 2H_2O$ (tri(μ-chloro)bis[tris(methoxydiphenylphosphane)-ruthenium(II)] chloride) are given in Table 2. The structure was solved by Patterson and refined by full-matrix least-squares on F^2 using the SHELXL-93 program [10,11]. Some atoms are highly agitated especially O301 and C302 which were refined isotropically.

3. Results and discussion

3.1. Synthesis

Classically, Ru(II)–phosphine complexes are prepared from the interaction of phosphines with a methanolic solution of $RuCl_3 \cdot 3H_2O$, under reflux [12]. However, a more convenient source material for Ru(II) complexes is the dichlorotetrakis(dmso)ruthenium(II) (**1**) easily obtained by refluxing $RuCl_3 \cdot 3H_2O$ in DMSO [9]. We used this complex as starting material for the preparation of dichlorotris(methoxydiphenylphosphane)ruthenium(II) (**3**) according to Scheme 1. The product was precipitated from ether solution, and recrystallized from methanol for the X-ray diffraction analysis.

3.2. NMR study

The complex was characterized, in $CDCl_3$ solution, by NMR analysis. The ^1H NMR spectrum showed a broad signal centered at 2.98 ppm due to the methoxy substituents and three groups of signals at 6.82 (m), 7.12 (br t), and 7.37 (br t) ppm, attributed to the phosphinite aromatic protons. In the free ligand **2**, the corresponding signals appeared at 3.65 (3H, d, J_{P-H} = 15 Hz), 7.33 (m, 6H) and 7.48 ppm (m, 4H). The ^{13}C NMR spectrum of the complex displayed a line at 55.1 ppm (OCH_3), three aromatic *C*-H lines at 126.77, 129.56, and 133.45 ppm, and one aromatic quaternary carbon line at 134.07 ppm. Comparatively, the free

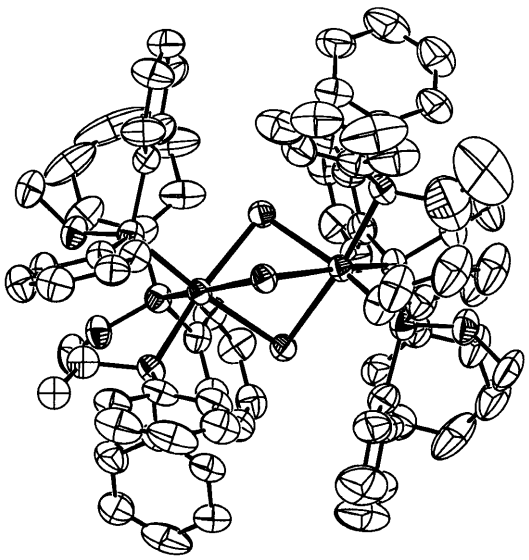


Fig. 1. Drawing [11] of the complex **4**, tri(μ-chloro)bis[tris(methoxydiphenylphosphane)ruthenium(II)] chloride. Displacement ellipsoids are at the 30% probability level. The Cl^- anion and the two co-crystallized water molecules are not represented.

ligand **2** showed a doublet at 56.65 ppm (OCH_3, J_{C-P} = 18.8 Hz), a doublet at 128.29 ppm (*C*H *meta*, J_{C-P} = 6.8 Hz), a singlet at 129.32 ppm (*C*H *para*), a doublet at 130.32 ppm (*C*H *ortho*, J_{C-P} = 21.3Hz), and a doublet at 132.05 ppm (quaternary C, J_{C-P} = 18.2 Hz). Thus, in the Ru(II) complex, the methoxy and part of the aromatic signals are shielded; a common feature of both ^1H and ^{13}C NMR spectra is the disappearance of the H–P and C–P couplings. The ^{31}P NMR spectrum showed no remaining free phosphinite, but the presence of a ruthenium-containing major compound which gives a single line at 136.9 ppm. All the previous NMR data are in good agreement with the presence, in $CDCl_3$ solution, of a symmetrical dimeric structure **4** (Scheme 1), as already proposed by Stephenson [13] who prepared **4** using another route. Traces of monomer **3** (and/or trimer) could be present because small lines at 138 and 139 ppm were visible in the ^{31}P NMR spectrum.

Table 1
Selected bond lengths (Å) and angles (°) in the complex

Ru(1)–P(4)	2.283(3)	Ru(2)–P(1)	2.268(3)
Ru(1)–P(5)	2.279(3)	Ru(2)–P(2)	2.274(3)
Ru(1)–P(6)	2.273(3)	Ru(2)–P(3)	2.287(3)
Ru(1)–Cl(1)	2.529(3)	Ru(2)–Cl(1)	2.529(3)
Ru(1)–Cl(2)	2.468(3)	Ru(2)–Cl(2)	2.461(3)
Ru(1)–Cl(3)	2.459(3)	Ru(2)–Cl(3)	2.468(3)
P(4)–Ru(1)–P(5)	92.8(1)	P(1)–Ru(2)–P(2)	93.6(1)
P(4)–Ru(1)–P(6)	90.1(1)	P(1)–Ru(2)–P(3)	89.5(1)
P(5)–Ru(1)–P(6)	94.1(1)	P(2)–Ru(2)–P(3)	92.1(1)
Cl(1)–Ru(1)–Cl(2)	77.4(1)	Cl(1)–Ru(2)–Cl(2)	77.5(1)
Cl(1)–Ru(1)–Cl(3)	77.9(1)	Cl(1)–Ru(2)–Cl(3)	77.7(1)
Cl(2)–Ru(1)–Cl(3)	80.6(1)	Cl(2)–Ru(2)–Cl(3)	80.6(1)
Ru(1)–P(4)–C(403)–C(404)	58(1)	Ru(2)–P(1)–C(103)–C(104)	62(1)
Ru(1)–P(4)–C(409)–C(410)	71(1)	Ru(2)–P(1)–C(109)–C(110)	59(1)
Ru(1)–P(4)–O(401)–C(402)	22(1)	Ru(2)–P(1)–O(101)–C(102)	15(1)
Ru(1)–P(5)–C(503)–C(504)	56(1)	Ru(2)–P(2)–C(203)–C(204)	70(1)
Ru(1)–P(5)–C(509)–C(510)	69(1)	Ru(2)–P(2)–C(209)–C(210)	57(1)
Ru(1)–P(5)–O(501)–C(502)	15(1)	Ru(2)–P(2)–O(201)–C(202)	17(1)
Ru(1)–P(6)–C(603)–C(604)	67(1)	Ru(2)–P(3)–C(303)–C(304)	49(1)
Ru(1)–P(6)–C(609)–C(610)	64(1)	Ru(2)–P(3)–C(309)–C(310)	72(1)
Ru(1)–P(6)–O(601)–C(602)	15(1)	Ru(2)–P(3)–O(301)–C(302)	35(1)

3.3. Crystal and molecular structure

The dimeric structure **4** of the complex in the solid state was confirmed by X-ray diffraction analysis (Table 2) of a single crystal (Fig. 1). Selected bond lengths and angles are presented in Table 1. The Ru–

Table 2
Crystal data and structure refinement

Formula	$Ru_2Cl_3(POC_{13}H_{13})_6^+ \cdot Cl^- \cdot 2H_2O$
Formula weight	1676.52
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	19.867(7)
b (Å)	17.835(6)
c (Å)	24.549(9)
α (°)	90
β (°)	99.10(3)
γ (°)	90
Volume (Å^3)	8589(5)
Z	4
D_{calc} (Mg m^{-3})	1.297
Absorption coefficient (mm^{-1})	0.374
$F(000)$	3400
Crystal size (mm)	$0.32 \times 0.24 \times 0.04$
θ Range for data collection (°)	2.59–21.94
Index ranges	$0 \le h \le 20$, $0 \le k \le 18$, $-25 \le l \le 25$
Reflections collected (MAR345)	37210 (60 img, $\Delta\phi$ 3°, 99.4% complete)
Independent reflections	10 363 ($R_{int} = 0.057$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10 362/3/730
Goodness-of-fit (all data)	1.069(1.155)
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0878$, $wR_2 = 0.2698$ (8174 observed)
R indices (all data)	$R_1 = 0.1037$, $wR_2 = 0.2842$
Largest difference peak and hole (e Å^{-3})	1.685 at 1.95 Å de Cl^- and −1.176

Table 3
Oxidation of alcohols catalyzed by Ru(II) complexes [a]

	Alcohol	Complex **4**		Complex **5**	
		Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
1	Benzyl alcohol	26	95	94	92
2	1-Octanol	22	100	95	80 [b]
3	2-Hexen-1-ol (*trans*)	13	100	90	100
4	2-Hexen-1-ol (*cis*)	25	100	100	100
5	1-Phenylethanol	24		70	
6	2-Octanol	21		100	

[a] Experimental conditions: the alcohols (10^{-3} mol) in CH_2Cl_2 (10 cm^3) were treated with NMMO (2 equiv.) and the catalyst (2 mol% relative to the alcohol) at 20°C during 6 h in the case of complex **4**, and during 1.5 h in the case of complex **5**.
[b] Results obtained after 30 min of reaction.

Ru distance, 3.387(2) Å, is in the range observed for other triply chloride-bridged diruthenium complexes [14]. The mean values for Ru–Cl and Ru–P bond lengths (Table 1) are 2.486 and 2.277 Å, respectively. A survey of the Cambridge Structural Database [15] revealed ten entries where the $(R_3P)_3Ru(\mu\text{-}Cl_3)Ru(PR_3)_3$ was present. For all these entries, R is an alkyl group. From these ten structures, we calculated means of 2.494 Å for Ru–Cl and 2.302 Å for Ru–P bond lengths, quite similar to the values observed in the title complex. As shown by the torsion angles Ru–P–C–C and Ru–P–O–C, the aromatic rings and the methoxy substituents of the six P atoms adopted nearly the same orientation. One of the two co-crystallized water molecules is hydrogen bonded to the oxygen atom of two methoxy groups of the same molecule: O_{700}–O_{101} = 3.06(1) Å and O_{700}–O_{201} = 3.00(1) Å (O_{101} and O_{201}: $-x$, $0.5+y$, $0.5-z$).

3.4. Catalytic activity

The catalytic performances of the Ru(II) complex **4** have been evaluated in a classical oxidation system [16] initially developed for the study of $RuCl_2(PPh_3)_3$ (**5**). Alcohols (10^{-3} mol), dissolved in dichloromethane (10 cm^3), were treated at room temperature with *N*-methylmorpholine oxide (NMMO, 2 equiv.) in the presence of the tested catalyst (2 mol%). The crude reaction mixtures were quantitatively analyzed by gas chromatography (entries 2, 3, 4, and 6; internal standard = tetradecane) and high performance liquid chromatography (entries 1 and 5), after 6 h of reaction with complex **4**, and 1.5 h of reaction with complex **5**. The conversion (percentage of transformed alcohol) and selectivity (percentage of aldehyde versus carboxylic acid; no other side-product was detected) are summarized in Table 3.

4. Conclusion

The dimeric complex **4** appeared less active than the reference complex **5** for which a monomeric structure has been established [17]. However, the catalyst **4** offers the advantage of giving higher selectivities; oxidation of primary aliphatic alcohols furnished the corresponding aldehydes without contamination by the carboxylic acid. Moreover, the complex **4** was more stable versus the oxidation than the commercial catalyst **5**. When examining by NMR a sample of **5** dissolved in $CDCl_3$ under air atmosphere, the progressive formation of triphenylphosphine oxide was visible within 24 h, resulting from the auto-oxidative destruction of the catalyst. On the contrary, complex **4** was perfectly stable under the same conditions. This interesting property led us to examine now the synthesis of Ru(II) complexes with tripodal phosphinite ligands susceptible to form more active monomeric complexes, and to be fixed further on solid supports.

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