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Electrosynthesis of binuclear ruthenium complexes from [$RuCl_3$(dppb)(L)] precursors [L = pyridine, 4-methylpyridine or dimethyl sulfoxide; dppb = 1,4-bis(diphenylphosphino)butane]

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Electrolysis has been examined as a method of synthesis for [(L)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] complexes, where dppb = 1,4-bis(diphenylphosphino)butane and L = pyridine (py), 4-methylpyridine (4-pic) or dimethyl sulfoxide (DMSO), by using [$RuCl_3$(dppb)(L)] as precursors. The products of the electrolysis were characterized by ^{31}P-{^{1}H} NMR, cyclic voltammetry and near infrared spectroscopy. The presence of the [Ru_2Cl_5(dppb)$_2$] complex in the electrochemical cell suggests a mechanism by which the starting original species from the bulk solution reacts with the reduced form [$RuCl_2$(dppb)(L)] generated at the surface of the electrode. The crystal structure of the precursor *mer*-[$RuCl_3$(dppb)(4-pic)] was determined by X-ray diffraction.

Introduction

The chemistry of ruthenium(II) complexes containing a single bis(phosphine) ligand per metal centre has been of interest because of its importance in catalytic hydrogenation reactions.[1–7] To develop new methodologies for the preparation of compounds containing the "$RuCl_2$(dppb)" core, we described recently the synthesis and characterization of [$RuCl_2$(dppb)(L)$_2$] complexes from either [$RuCl_2$(dppb)(PPh_3)] or [{$RuCl_2$(dppb)}$_2$(μ-dppb)] where dppb = $Ph_2P(CH_2)_4PPh_2$ and L = N-donor ligands.[8]

The ruthenium complex [Ru_2Cl_4(BINAP)$_2$(NEt_3)] [BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] has been successively used as a catalyst for the asymmetric hydrogenation of several prochiral substrates.[9–12] This type of complex, with 1,4-bis(diphenylphosphino)butane, exhibits the general formula [Ru_2Cl_4(dppb)$_2$(L)] or [(L)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)], where L = NEt_3, pyridine, acetone, acetophenone, dimethyl sulfoxide, dimethyl sulfide, tetramethylene sulfoxide or tetrahydrothiophene. They form from [$RuCl_2$(dppb)(PPh_3)] or [Ru_2Cl_4(dppb)$_2$] on reaction with the respective ligands.[4,7]

In this work we present a new and effective route for the synthesis of triply bridged binuclear complexes of the type [(L)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)], by reductive electrolysis of [$RuCl_3$(dppb)(L)], where L = pyridine (py), 4-methylpyridine (4-pic) or dimethyl sulfoxide (DMSO).

Experimental

Chemicals employed in this work were of reagent-grade quality (Aldrich). Tetrabutylammonium perchlorate (Fluka purum) was recrystallized from ethanol–water and dried overnight, under vacuum, at 100 °C. Reagent-grade solvents (Merck) were appropriately distilled, dried and stored over Linde 4 Å molecular sieves. Purified argon was used for the removal of dissolved oxygen. IR spectra were recorded from CsI pellets on a Bomen-Michelson 102 instrument, UV/Vis spectra in CH_2Cl_2 with a HP 8452 A spectrophotometer and ^{31}P-{^{1}H} NMR spectra in CH_2Cl_2 solution at room temperature with a Bruker 400 MHz spectrometer (161 MHz) with the chemical shifts reported relative to H_3PO_4 (85%). Cyclic voltammetric measurements were carried out at room temperature in freshly distilled CH_2Cl_2 containing 0.1 mol l^{-1} $Bu_4N^+ClO_4^-$, using an EG&G/PARC electrochemical system consisting of a 273A potentiostat or BAS 100B Electrochemical Analyzer. A three-electrode system with resistance compensation was used throughout. The working and auxiliary electrodes were a stationary platinum foil and a wire, respectively. The reference electrode was Ag/AgCl in a Luggin capillary, 0.1 mol L^{-1} NBu_4ClO_4 in CH_2Cl_2, a medium in which ferrocene is oxidized at 0.43 V *vs.* Fc$^+$/Fc; all potentials are referred to this electrode. In controlled-potential electrolysis a platinum mesh was used as working electrode and the auxiliary electrode was separated from the solution by a sintered-glass disk. Elemental analyses were performed at the Institute of Chemistry of the University of São Paulo, São Paulo.

Complexes with general formula [$RuCl_3$(dppb)(L)] were all obtained by using the same procedure. Thus [$RuCl_3$(dppb)(4-pic)] was prepared from [$RuCl_3$(dppb)]·[H_2O][14] (0.100 g, 1.53 mmol) and 4-methylpyridine (31 μl, 3.21 mmol) in dichloromethane (10 ml) with stirring at room temperature for 12 h. The volume of the resulting red–orange solution was reduced to *ca.* 1 ml and diethyl ether added to precipitate a red–orange solid which was filtered off, washed well with ether and dried under vacuum. Suitable crystals for X-ray analysis were grown by slow evaporation of a dichloromethane–diethyl ether solution. Yield: 0.087 g (78%). Calc. for $C_{34}H_{35}Cl_3NP_2Ru$: C, 56.17; H, 4.85; N, 1.93%. Found: C, 56.21; H, 5.06; N, 1.99%.

For the [$RuCl_3$(dppb)(py)] complex: Yield 0.10 g (91.43%). Calc. for $C_{33}H_{33}Cl_3NP_2Ru$: C, 55.59; H, 4.66; N, 1.96%. Found:

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C, 55.63; H, 4.71; N, 1.91%. The synthesis of [$RuCl_3$(dppb)-(DMSO)] is reported elsewhere.[13]

X-Ray diffraction analysis of [$RuCl_3$(dppb)(4-pic)]

A red prismatic crystal of the complex was used in the single-crystal X-ray diffraction experiment. All measurements were made on a Enraf-Nonius CAD-4 diffractometer with graphite monochromated Cu-Kα ($\lambda = 1.54184$ Å) radiation. Unit cell parameters and orientation matrices for data collection were obtained from a least-squares refinement using the setting angles of 25 reflections in the θ range 11–30°. The data were collected in the ω–2θ scan mode. One standard reflection was measured every 30 min and used to apply a decay correction. The maximum decay was 2%. The data collection and reduction were performed with the programs CAD 4[14] and XCAD 4,[15] respectively. A numerical absorption correction[16] implemented in the program PLATON[17] was applied.

The structure was solved by direct methods with SHELXS 86.[18] The Fourier map obtained showed all non-hydrogen atoms. The model was refined by a full-matrix least-squares procedure on F^2 by means of SHELXL 93.[19] After inclusion of the complete complex in the refinement, the Fourier-difference map showed several peaks near the inversion center at ($\frac{1}{2}$, 0, $\frac{1}{2}$). They were interpreted as a CH_2Cl_2 solvent molecule with just one half per asymmetric unit. The disorder was modeled including four chlorine atoms and a carbon atom, which could be interpreted as an independent CH_2Cl_2 molecule in two different positions: C(1s), Cl(1s) and Cl(2s); and C(1s), Cl(3s) and Cl(4s), respectively. The hydrogen atoms of the aromatic rings and CH_2 were set isotropic with a thermal parameter 20% greater than the equivalent isotropic displacement parameter of the carbon atom to which each one is bonded; this percentage was set to 50% for the hydrogen atoms of the methyl group. All hydrogen atoms were stereochemically positioned and refined with the riding model.[19] The C–H bond lengths in the aromatic rings, CH_2 and CH_3 groups were set equal to 0.93, 0.97 and 0.96 Å, respectively. The aromatic rings were treated as rigid groups and all non-H atoms refined anisotropically, with the exception of the disordered solvent atoms. Atomic scattering factors were taken from ref. 20.

The X-ray data collection and experimental details are summarized in Table 1 and relevant interatomic distances and angles are listed in Table 2.

CCDC reference number 186/2132.

See http://www.rsc.org/suppdata/dt/b0/b001422m/ for crystallographic files in .cif format.

Results and discussion

IR spectra of the [$RuCl_3$(dppb)(4-pic)] complex show the typical bands of the coordinated phosphine ligand at 1485, 1096, 1000 and 513 (ν_{P-C}), 696 (γ_{C-H}), 332 (ν_{P-C}) and 274 cm^{-1} (ν_{Ru-Cl}).[8] An absorption at 435 cm^{-1} can tentatively be attributed to (ν_{Ru-N}).[21] The EPR spectrum shows g values ($g_1 = 2.487$; $g_2 = 2.101$; $g_3 = 1.866$) (Fig. 1) typical for complexes with strong rhombic distortions. For the complex with the pyridine ligand these are $g_1 = 2.928$, $g_2 = 2.037$ and $g_3 = 1.607$.

Fig. 2 is an ORTEP[22] view of [$RuCl_3$(dppb)(4-pic)]. The asymmetric unit consists of one [$RuCl_3$(dppb)(4-pic)] and half a CH_2Cl_2 molecule. The ruthenium(III) ion is in a distorted octahedral environment; two phosphorus atoms, a chloride and a nitrogen atom of the 4-methylpyridine group form an equatorial plane; two other chlorides are in mutually *trans* positions, slightly bending toward the 4-methylpyridine group. The Ru–Cl distances (*ca.* 2.3 Å) are in the normal range for ruthenium(III) complexes.[23,24] The Ru–P(2) distance, slightly longer than the Ru–P(1) in the 4-methylpyridine complex (Table 2), can be attributed to the better σ-donor properties of the chloride with regard to the pyridine ring from the ligand *trans* to the phosphorus atoms. The distance Ru–P(1) is similar to the length, 2.326(2) Å,[23] found in *mer*-[$RuCl_3(PPh_3)(MeIm)_2$] (MeIm = 1-methylimidazole) where the PPh_3 is *trans* to the methylimidazole.

Cyclic voltammetric measurements of [$RuCl_3$(dppb)(4-pic)] in CH_2Cl_2 (Fig. 3) reveal an irreversible $Ru^{III} \longrightarrow Ru^{II}$ process [$E_{pc} = -0.08$ V]. Our electrochemical data suggest that binuclear [$Ru_2Cl_4(dppb)_2$(4-pic)] and [$Ru_2Cl_5(dppb)_2$] are formed in solution according to reactions (2) and (3), which compete with each other and with (4).

Table 1 Crystal data and structure refinement of the [$RuCl_3$(dppb)-(4-pic)] complex

Color/shape	Red/prism
Empirical formula	$C_{34}H_{35}Cl_3NP_2Ru{\cdot}0.5CH_2Cl_2$
Formula weight	768.95
T/K	293(2)
Crystal system	Orthorhombic
Space group	*Pbca*
a/Å	14.785(10)
b/Å	17.559(5)
c/Å	27.448(5)
V/Å^3	7125.8(54)
Z	8
μ/mm^{-1}	7.356
Reflections collected	6567
Independent/observed reflections	6194 [$R_{int} = 0.0829$]/2213 [$I < 2\sigma(I)$]
Data/restraints/parameters	6191/1/345
Final $R1$, $wR2$ indices [$I > 2\sigma(I)$]	0.0565, 0.1228
(all data)	0.2352, 0.1589

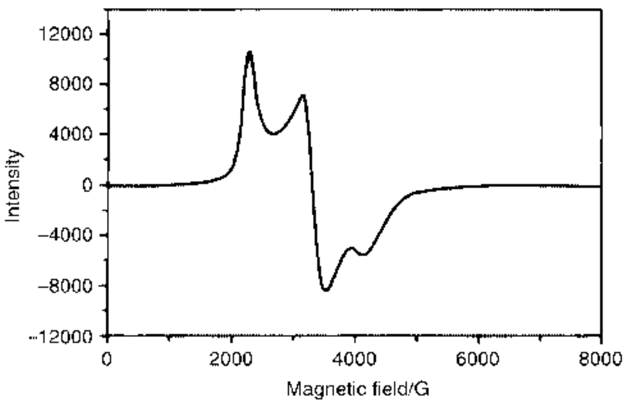

Fig. 1 EPR spectrum of [$RuCl_3$(dppb)(4-pic)] (X band frequency) at −160 °C in the solid state.

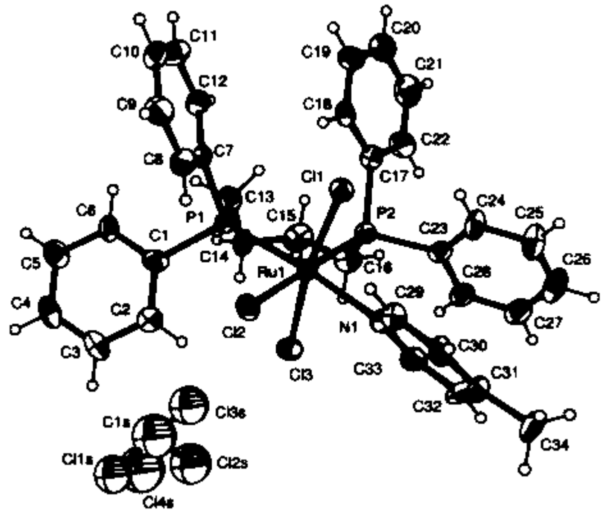

Fig. 2 An ORTEP view of the asymmetric unit of [$RuCl_3$(dppb)-(4-pic)], showing the atom labeling and 30% probability ellipsoids.

Table 2 Selected bond lengths [Å] and angles [°] for the [RuCl$_3$(dppb)(4-pic)] complex, e.s.d.s in parentheses

Ru(1)–P(1)	2.329(3)	P(1)–C(13)	1.838(11)
Ru(1)–P(2)	2.413(3)	P(2)–C(16)	1.828(11)
Ru(1)–N(1)	2.209(9)	P(2)–C(17)	1.839(6)
Ru(1)–Cl(1)	2.327(3)	P(2)–C(23)	1.825(6)
Ru(1)–Cl(2)	2.372(3)	N(1)–C(33)	1.331(12)
Ru(1)–Cl(3)	2.344(3)	N(1)–C(29)	1.367(12)
P(1)–C(1)	1.843(7)	C(29)–C(30)	1.379(14)
P(1)–C(7)	1.840(6)		
P(1)–Ru(1)–P(2)	92.59(11)	Cl(1)–Ru(1)–Cl(3)	170.84(11)
P(1)–Ru(1)–Cl(2)	88.80(11)	Cl(2)–Ru(1)–P(2)	177.94(10)
P(1)–Ru(1)–Cl(3)	92.97(11)	Cl(3)–Ru(1)–Cl(2)	93.14(10)
N(1)–Ru(1)–P(1)	172.9(2)	Cl(3)–Ru(1)–P(2)	88.30(10)
N(1)–Ru(1)–P(2)	94.4(2)	C(33)–N(1)–C(29)	116.7(10)
N(1)–Ru(1)–Cl(1)	86.1(2)	C(33)–N(1)–Ru(1)	124.7(8)
N(1)–Ru(1)–Cl(2)	84.2(2)	C(29)–N(1)–Ru(1)	118.6(7)
N(1)–Ru(1)–Cl(3)	86.5(2)	C(13)–P(1)–C(7)	103.9(5)
Cl(1)–Ru(1)–P(1)	95.00(10)	C(13)–P(1)–C(1)	99.4(4)
Cl(1)–Ru(1)–P(2)	86.84(9)	C(13)–P(1)–Ru(1)	116.7(4)
Cl(1)–Ru(1)–Cl(2)	91.54(9)	C(7)–P(1)–Ru(1)	114.6(3)
C(1)–P(1)–Ru(1)	119.2(3)	C(32)–C(31)–C(30)	116.0(11)
C(23)–P(2)–Ru(1)	111.1(3)	C(32)–C(31)–C(34)	122.8(14)
C(16)–P(2)–Ru(1)	115.3(4)	C(30)–C(31)–C(34)	121.2(14)
C(17)–P(2)–Ru(1)	121.6(3)	C(33)–C(32)–C(31)	120.6(11)
C(29)–C(30)–C(31)	120.5(12)	N(1)–C(33)–C(32)	123.7(12)

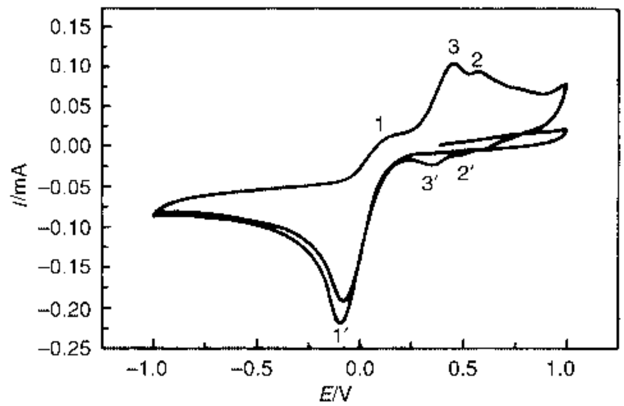

Fig. 3 Cyclic voltammograms of [RuCl$_3$(dppb)(4-pic)], 1.0 × 10^{-3} mol l^{-1}, in CH$_2$Cl$_2$ with 0.1 mol l^{-1} NBu$_4$ClO$_4$, scan rate 100 mV s^{-1}, measured at a platinum electrode.

$$[\mathrm{RuCl_3(dppb)(4\text{-}pic)}] + e^- \longrightarrow \text{“}\mathrm{RuCl_2(dppb)(4\text{-}pic)}\text{”} + \mathrm{Cl^-} \qquad (1)$$

$$[\mathrm{RuCl_3(dppb)(4\text{-}pic)}] + \text{“}\mathrm{RuCl_2(dppb)(4\text{-}pic)}\text{”} \longrightarrow \mathrm{Ru_2Cl_5(dppb)_2} + 2\ (4\text{-}\mathrm{pic}) \qquad (2)$$

$$2\ \text{“}\mathrm{RuCl_2(dppb)(4\text{-}pic)}\text{”} \longrightarrow \mathrm{Ru_2Cl_4(dppb)_2(4\text{-}pic)} + 4\text{-}\mathrm{pic} \qquad (3)$$

$$\text{“}\mathrm{RuCl_2(dppb)(4\text{-}pic)}\text{”} + 4\text{-}\mathrm{pic} \longrightarrow \mathrm{RuCl_2(dppb)(4\text{-}pic)_2} \qquad (4)$$

To pursue this hypothesis further, we electrolysed (at −0.30 V) 50% (based on current passing) of the content (0.02 g in 10 ml of CH$_2$Cl$_2$ 0.1 mol l^{-1} NBu$_4$ClO$_4$) of [RuCl$_3$(dppb)(4-pic)] complex. The electrolysed solution was evaporated and the solid formed extracted with CCl$_4$ (10 ml), resulting in a red solution and a pale yellow solid (9.7 mg; mixture of mono and binuclear ruthenium(II) complexes). This solid was separated by filtration and the red solution collected and concentrated to 1 ml; addition of hexane (10 ml) yielded a bright red solid (0.6 mg, 3.47%; based on Ru). The red solid was characterized as a mixed valence complex [Ru$_2$Cl$_5$(dppb)$_2$] by UV/Vis/Near IR, cyclic voltammetry and EPR as described elsewhere.[13,24]

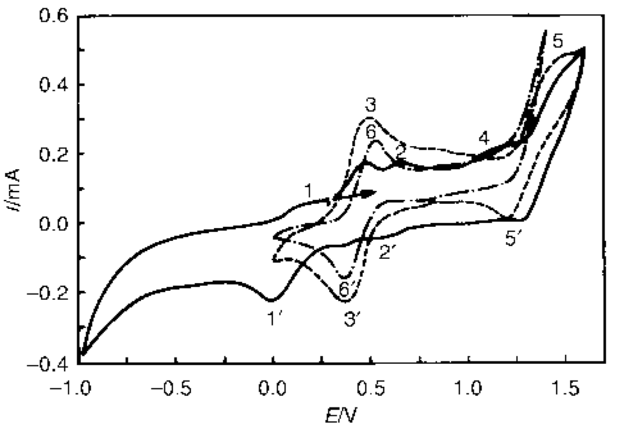

Fig. 4 Cyclic voltammograms of the electrolysis product of [RuCl$_3$(dppb)(4-pic)] at −0.30 V in CH$_2$Cl$_2$ in NBu$_4$ClO$_4$, scan rate 100 mV s^{-1}, 50% of the content, (——) of [Ru$_2$Cl$_4$(dppb)$_2$(4-pic)] (–––) and of *trans*-[RuCl$_2$(dppb)$_2$(4-pic)$_2$] monomer (–·–).

The ^{31}P-{^{1}H} NMR spectrum of the yellow solid in CH$_2$Cl$_2$ shows a singlet at δ 40.5 and two independent AB quartets centred at δ_A 54.80 and δ_B 45.93 ($J_{AB} = 37$), δ_C 52.38 and δ_D 51.94 ($J_{CD} = 43$ Hz). The singlet signal was attributed to [RuCl$_2$(dppb)(4-pic)$_2$] confirmed by independent synthesis.[8] The two AB quartet patterns were attributed to the presence of [Ru$_2$Cl$_4$(dppb)$_2$(4-pic)]. To confirm this the complex was chemically generated from [RuCl$_2$(dppb)(PPh$_3$)] as described for other ligands such as amine, dimethyl sulfoxide or carbon monoxide.[4] It was characterized by microanalysis, ^{31}P-{^{1}H} NMR and cyclic voltammetry. The data obtained were the same as for the [Ru$_2$Cl$_4$(dppb)$_2$(4-pic)] complex obtained electrochemically as described above. The cyclic voltammogram of the electrolysis product is shown in Fig. 4. In this cyclic voltammogram it is possible to detect the presence of the mixed valence complex [Ru$_2$Cl$_5$(dppb)$_2$] (peaks 1-1′,2-2′) [$E_{pa}(1) = 0.13$ and $E_{pc}(1') = -0.01$; $E_{pa}(2) = 0.65$ and $E_{pc}(2') = 0.60$ V].[13] There are peaks that certainly belong to binuclear [Ru$_2$Cl$_4$(dppb)$_2$(4-pic)] (peaks 3-3′,5-5′) [$E_{pa}(3) = 0.48$ and $E_{pc}(3') = 0.36$; $E_{pa}(5) = 1.47$ and $E_{pc}(5') = 1.28$ V]. These values are in agreement with those found for the respective species isolated chemically (Fig. 4). The cyclic voltammogram of the monomer [RuCl$_2$(dppb)(4-pic)$_2$] (Fig. 4) shows an electrochemical process (peaks 6-6′) coincident with one of those mentioned above ($E_{pa} = 0.51$ and $E_{pc} = 0.36$ V).[8]

Exhaustive electrolysis of [RuCl$_3$(dppb)(4-pic)] at −0.3 V produces only a triply bridged complex, whose identity has previously been confirmed as [Ru$_2$Cl$_4$(dppb)$_2$(4-pic)] (0.170 g, 94%) (Fig. 4). The same results were achieved for [RuCl$_3$(dppb)(py)] and [RuCl$_3$(dppb)(DMSO)]. The electrochemical process at about 1.18 V in the electrolysed mixture is due to the oxidation of chloride.[25]

The compounds [Ru$_2$Cl$_4$(dppb)$_2$(DMSO)] and [Ru$_2$Cl$_4$(dppb)$_2$(py)] were obtained similarly by electrolysis from the corresponding [RuCl$_3$(dppb)(L)] complexes and authenticated by their known ^{31}P-{^{1}H} NMR data.[4]

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