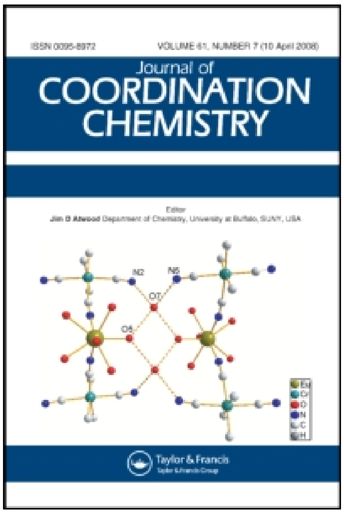

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A TRICHLORO-BRIDGED DIRUTHENIUM (II, III) COMPLEX: PREPARATION, PROPERTIES AND X-RAY STRUCTURE OF TRI(-μ-CHLORO) DICHLOROCARBONYLTRIS (TRIPHENYLPHOSPHINE)DIRUTHENIUM(II, III)

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A TRICHLORO-BRIDGED DIRUTHENIUM (II,III) COMPLEX: PREPARATION, PROPERTIES AND X-RAY STRUCTURE OF TRI(-μ-CHLORO) DICHLOROCARBONYLTRIS (TRIPHENYLPHOSPHINE)DIRUTHENIUM(II,III)

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The triply chloro-bridged binuclear complex $[Ru_2Cl_5(CO)(PPh_3)_3]\cdot CH_2Cl_2$, ($PPh_3$ = triphenylphosphine), $M_r = 1279.23$, prepared from the precursor compound $[RuCl_3(PPh_3)_2DMA]\cdot DMA$ (DMA = *N,N'*-dimethylacetamide) and crystallizes in the monoclinic space group $P2_1/c$. The structure was solved from 6994 independent reflections for which $I > 3\sigma(I)$ by Patterson and difference Fourier techniques and refined to a final $R = 0.042$. The complex is formed by two Ru atoms bridged through three chloride anions. One Ru atom is further coordinated to two non-bridging Cl atoms and a triphenylphosphine ligand, whereas the other is bonded to two PPh_3 ligands and a carbon monoxide molecule. The presence of Ru^{III} was confirmed by EPR data. The absence of an intervalence charge-transfer transition (IT) in the near-infrared spectrum suggests that the binuclear complex is of a localized valence type. The IR spectrum shows a ν_{CO} band at 1964 cm^{-1} and $\nu_{Ru\text{-}Cl}$ bands at 328, 280 cm^{-1}, corresponding to chlorides at terminal positions and 250, 225 cm^{-1} for the bridged ones. Two redox processes, Ru^{II}/Ru^{II} ($E_{1/2} = -0.29$ V) $\leftarrow Ru^{II}/Ru^{III} \rightarrow$ ($E_{1/2} = 1.19$ V) Ru^{III}/Ru^{III}, were observed by cyclic voltammetry.

KEYWORDS: Binuclear ruthenium (II,III) complex, triphenylphosphine, carbon monoxide; X-ray structure, spectroscopical measurements, electrochemistry

INTRODUCTION

Since the discovery of the $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{5+}$ compound by Creutz and Taube,[1] extensive studies of mixed-valence ruthenium complexes have been reported. Our previous studies[2,3] have shown that the reactivity of the precursor

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complex, $[RuCl_3(PPh_3)_2DMA]\cdot DMA$ (**1**), leads to different products depending on reaction conditions. The title compound, $[Ru_2Cl_5(CO)(PPh_3)_3]\cdot CH_2Cl_2$, was obtained from the reaction of (**1**) with CO(g). Stephenson and co-workers[4] reported analogous species of this complex and from electrochemical studies of the triply-bridged diruthenium complexes having general formula $[Ru_2Cl_5YL_3]$ (L = P(*n*-tol)$_3$, PPh$_3$, and Y = CO or CS), they proposed, for the carbon monoxide complex, the configuration shown in Figure 1.

Our particular interest in this class of compounds is in the study of the characteristics of the redox potentials of metal ions when they are bound to σ or π ligands, in order to eventually identify the localization of electrons in the metallic centres. This work led to the discovery of a new reaction for the starting material, $[RuCl_3(PPh_3)_2DMA]\cdot DMA$, and this paper describes the synthesis and characterization of the binuclear complex $[Ru_2Cl_5(CO)(PPh_3)_3]\cdot CH_2Cl_2$.

EXPERIMENTAL

General

All solutions were prepared under a pre-purified argon purge and were kept under an argon blanket during the experiments. All solvents were purified following previously described procedures[5] and stored over Linde 4 Å molecular sieves. Triphenylphosphine (Aldrich) was used as supplied. The primary ruthenium source was $RuCl_3\cdot 3H_2O$ (Degussa S/A). The precursor compound, $[RuCl_3(PPh_3)_2DMA]\cdot DMA$, was prepared as mentioned in the literature.[6]

Tri(-μ-chloro)-dichlorocarbonyltris(triphenylphosphine)-diruthenium(II,III) dichloromethane solvate

The synthesis of the title complex follows the procedure applied by Ruiz-Ramirez *et al.*[7] in the preparation of *trans*-$[RuCl_2(CO)_2(PPh_3)_2]$ from $[RuCl_3(PPh_3)_2S]$, where S = MeOH or $MeNO_2$: carbon monoxide was bubbled through a suspension of $[RuCl_3(PPh_3)_2DMA]\cdot DMA$ (0.2 g – 0.22 mol) in 2 cm^3 of benzene for 30 min at room temperature. The volume of the resulting brown solution was reduced to *ca* 0.8 cm^3, after which cold, deoxygenated ethanol was added. The yellow resulting solid (yield: 75%) was filtered and thoroughly washed with ethanol, hexane and

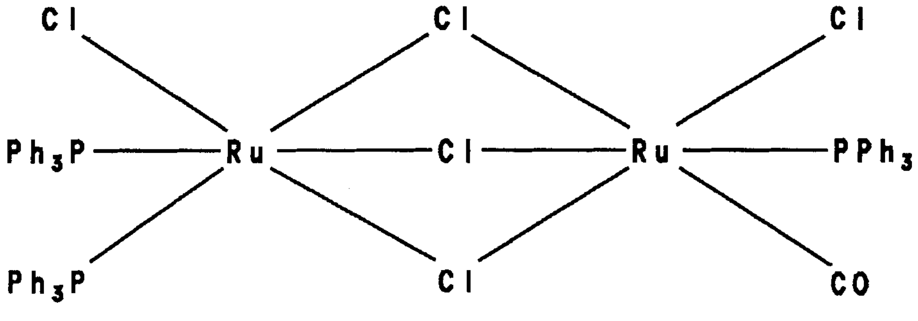

Figure 1 Suggested structure for the $[Ru_2Cl_5(CO)(PPh_3)_3]$ complex (after Stephenson *et al.*[4]).

diethyl ether. Recrystallization from dichloromethane/ethanol/diethyl ether produced air-stable, brownish-red crystals. Anal; calc. for $C_{56}H_{47}Cl_7OP_3Ru_2$: C, 52.58; H, 3.70%. Found : C, 53.33; H, 3.71%.

X-ray diffraction data

A complete data set was collected on an Enraf-Nonius CAD-4 four-circle diffractometer, from a prismatic crystal. Cell dimensions and the orientation matrix were calculated by least-squares methods from 25 centred reflections. Diffraction intensities were measured by the ω-2θ scan technique using a variable scan speed between 6.7–20.0° min^{-1} determined by a pre-scan at 20.0° min^{-1}. The intensity of one standard reflection was essentially constant over the duration of the experiments. Data were corrected for Lorentz, polarization and absorption effects, following the procedure of Walker and Stuart.[8] Merging of the 9021 intensity measurements resulted in 8752 independent reflections with an internal consistency index (Sheldrick[9]) R_{int} = 0.015. The 6994 reflections having $I > 3\sigma(I)$ were used for the structure determination and refinement, performed with the SHELX-76[9] and MolEN[10] systems of programs. Bonded H-atom scattering factors (Stewart, Davidson and Simpson[11]) and complex scattering factors (Cromer and Mann;[12] Cromer and Liberman[13]) for the remaining atoms were employed. The molecular drawing (Figure 2) was produced with the program ORTEP.[14]

Crystal structure determination and refinement

The structure was solved by standard Patterson and difference Fourier techniques and refined by full-matrix least-squares methods. The phenyl rings were treated as rigid groups and all non-hydrogen atoms were refined with anisotropic temperature factors. The phenyl hydrogen atoms were located at calculated positions and

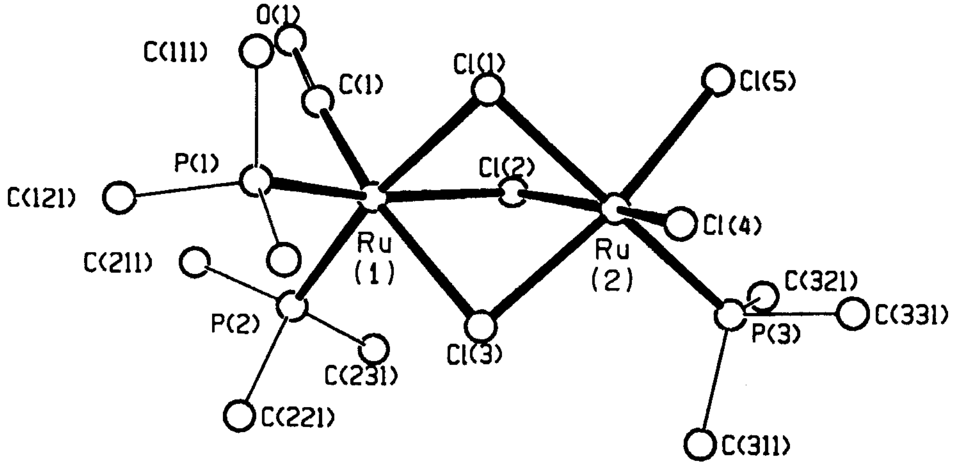

Figure 2 Perspective view of the X-ray structure of the binuclear complex $[Ru_2Cl_5(CO)(PPh_3)_3]\cdot CH_2Cl_2$, with all phenyl rings and solvated dichloromethane molecule omitted for clarity.

included as fixed contributors, with a common isotropic temperature factor of 5 Å^2. Absorption corrections were applied following the procedure of Walker and Stuart[8] with minimum and maximum transmission factors of 0.889 and 1.146, respectively. The maximum value of Δ/σ in the final refinement cycle was 0.07. Crystal data and refinement details are given in Table 1. Atomic coordinates and equivalent isotropic temperature factors for all non-H atoms are given in Table 2. Corresponding interatomic bond distances and angles, excluding those of the phenyl rings which were refined as rigid groups, are given in Table 3. Listings of anisotropic thermal parameters, hydrogen atoms coordinates, bond distances and angles of all phenyl rings and the observed and calculated structure factors are available from the the authors upon request.

Spectroscopic measurements

Pellets were prepared from crystalline powder samples diluted in CsI. IR spectra were performed on a Bomem-Michelson 102 spectrophotometer in the region 4000–200 cm^{-1}. For near-IR spectra, a Cary 2315 spectrophotometer and matched anaerobic quartz cells were employed. The electronic spectrum was measured in $CDCl_3$ solution (2.6 × 10^{-3} M) and recorded on a Cary 2315 spectrophotometer.

Table 1 Crystal data, data collection details and structure refinement results for $[Ru_2Cl_5(CO)(PPh_3)_3]\cdot CH_2Cl_2$.

formula	$[Ru_2Cl_5(CO)(PPh_3)_3]\cdot CH_2Cl_2$
mol wt	1279.23
space group	$P2_1/c$
lattice parameters	
a	14.600(3)
b	18.254(3)
c	20.52(1)Å
β	99.46(3)°
V	5394(5)Å
Z	4
D(calc)	1.575 g·cm^{-3}
crystal dimensions	0.12 × 0.30 × 0.60 mm
radiation	MoKα, λ = 0.71073Å
T	25°C
linear abs coeff (μ)	9.283 cm^{-1}
scan technique	ω–2θ
scan speed range	6.7–20° min^{-1}
θ range for data collect	0–25°
F(000)	2548
no. ind. reflns.	8752
no. reflns. above $3\sigma(I)$	6994
no. refined parameters	514
minimized function	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
weighting scheme	$w = [\sigma^2(\lvert F_o\rvert) + 0.00025\lvert F_o\rvert^2]^{-1}$
$R = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$	0.042
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.046
$S = [\Sigma w(\lvert F_o\rvert - \lvert F_o\rvert)^2/(M-N)]^{1/2}$	1.92
h_{min}, h_{max}; k_{min}, k_{max}; l_{min}, l_{max}	– 17, 17; 0, 21; 0, 24
max, min residual ρ	0.95, – 1.14 eÅ^{-3}

Table 2 Fractional Atomic Coordinates and Isotropic Temperature Parameters (Å^2) for [$Ru_2Cl_5(CO)(PPh_3)_3$]·CH_2Cl_2

Atom	X/A	Y/B	Z/C	B_{iso}	Atom	X/A	Y/B	Z/c	B_{iso}
Ru(1)	0.13313(3)	0.10400(2)	0.22552(2)	1.98(1)	C(213)	-0.1435(2)	0.1133(2)	0.3578(2)	3.9(2)
Ru(2)	0.32507(3)	0.04848(2)	0.17373(2)	2.29(1)	C(214)	-0.1379(2)	0.0936(2)	0.4241(2)	4.4(2)
Cl(1)	0.1635(1)	0.0642(1)	0.1165(1)	2.73(4)	C(215)	-0.0514(2)	0.0833(2)	0.4634(2)	4.3(2)
Cl(2)	0.2387(1)	-0.0015(1)	0.2559(1)	2.94(4)	C(216)	0.0295(2)	0.0925(2)	0.4364(2)	3.6(2)
Cl(3)	0.2873(1)	0.1616(1)	0.2285(1)	2.61(4)	C(221)	0.1517(3)	0.2288(2)	0.3636(2)	3.2(2)
Cl(4)	0.3761(1)	0.1199(1)	0.0890(1)	7.07(8)	C(222)	0.1124(3)	0.2551(2)	0.4165(2)	4.5(2)
Cl(5)	0.3350(2)	-0.0712(2)	0.1261(1)	9.1(1)	C(223)	0.1265(3)	0.3277(2)	0.4366(2)	6.2(3)
P(1)	0.0414(1)	0.1991(1)	0.1701(1)	2.26(4)	C(224)	0.1800(3)	0.3741(2)	0.4038(2)	8.4(4)
P(2)	0.1297(1)	0.1341(1)	0.3363(1)	2.44(4)	C(225)	0.2194(3)	0.3478(2)	0.3510(2)	9.7(5)
P(3)	0.4757(1)	0.0335(1)	0.2255(1)	2.81(4)	C(226)	0.2052(3)	0.2752(2)	0.3309(2)	6.1(3)
C(1)	0.0333(4)	0.0444(3)	0.2249(3)	2.8(2)	C(231)	0.2184(3)	0.0823(2)	0.3900(2)	3.5(2)
O(1)	-0.0252(3)	0.0019(2)	0.2259(2)	4.6(2)	C(232)	0.2040(3)	0.0080(2)	0.4010(2)	4.8(2)
Cl(6)	0.6524(3)	0.2336(2)	0.0359(2)	13.5(2)	C(233)	0.2721(3)	-0.0328(2)	0.4411(2)	7.2(4)
Cl(7)	0.4654(3)	0.2320(3)	-0.0323(2)	18.7(3)	C(234)	0.3546(3)	0.0006(2)	0.4701(2)	8.0(4)
C(2)	0.5539(7)	0.1781(6)	0.0052(7)	11.2(5)	C(235)	0.3690(3)	0.0749(2)	0.4591(2)	7.8(4)
C(111)	-0.0234(2)	0.1708(2)	0.0890(1)	2.7(2)	C(236)	0.3009(3)	0.1157(2)	0.4191(2)	5.3(3)
C(112)	-0.0466(2)	0.0979(2)	0.0745(1)	3.2(2)	C(311)	0.5235(3)	0.1057(2)	0.2828(2)	3.2(2)
C(113)	-0.0976(2)	0.0796(2)	0.0132(1)	4.1(2)	C(312)	0.5221(3)	0.1767(2)	0.2572(2)	4.0(2)
C(114)	-0.1255(2)	0.1342(2)	-0.0336(1)	5.2(3)	C(313)	0.5670(3)	0.2332(2)	0.2954(2)	4.7(2)
C(115)	-0.1024(2)	0.2072(2)	-0.0191(1)	5.2(3)	C(314)	0.6133(3)	0.2188(2)	0.3592(2)	5.1(3)
C(116)	-0.0513(2)	0.2255(2)	0.0423(1)	3.9(2)	C(315)	0.6146(3)	0.1479(2)	0.3848(2)	5.5(3)
C(121)	-0.0520(2)	0.2421(2)	0.2069(2)	2.8(2)	C(316)	0.5697(3)	0.0913(2)	0.3466(2)	4.4(2)
C(122)	-0.0312(2)	0.2891(2)	0.2606(2)	3.6(2)	C(321)	0.5003(3)	-0.0502(2)	0.2738(2)	3.3(2)
C(123)	-0.1028(2)	0.3200(2)	0.2889(2)	4.6(2)	C(322)	0.5725(3)	-0.0970(2)	0.2644(2)	4.2(2)
C(124)	-0.1950(2)	0.3037(2)	0.2634(2)	5.6(3)	C(323)	0.5927(3)	-0.1585(2)	0.3047(2)	5.4(3)
C(125)	-0.2158(2)	0.2567(2)	0.2096(2)	5.3(3)	C(324)	0.5407(3)	-0.1732(2)	0.3545(2)	5.3(3)
C(126)	-0.1443(2)	0.2258(2)	0.1814(2)	3.9(2)	C(325)	0.4685(3)	-0.1264(2)	0.3640(2)	5.3(3)
C(131)	0.1084(2)	0.2762(2)	0.1448(2)	3.0(2)	C(326)	0.4483(3)	-0.0649(2)	0.3236(2)	4.3(2)
C(132)	0.1731(2)	0.2598(2)	0.1040(2)	3.5(2)	C(331)	0.5620(3)	0.0303(2)	0.1695(2)	3.6(2)
C(133)	0.2205(2)	0.3161(2)	0.0776(2)	4.5(2)	C(332)	0.6488(3)	0.0628(2)	0.1882(2)	7.8(4)
C(134)	0.2031(2)	0.3889(2)	0.0921(2)	5.3(3)	C(333)	0.7137(3)	0.0617(2)	0.1453(2)	10.0(5)
C(135)	0.1384(2)	0.4054(2)	0.1329(2)	5.7(3)	C(334)	0.6918(3)	0.0281(2)	0.0838(2)	7.9(4)
C(136)	0.0911(2)	0.3490(2)	0.1593(2)	4.2(2)	C(335)	0.6050(3)	-0.0044(2)	0.0651(2)	7.6(4)
C(211)	0.0239(2)	0.1121(2)	0.3701(2)	2.7(2)	C(336)	0.5401(3)	-0.0033(2)	0.1080(2)	6.2(3)
C(212)	-0.0626(2)	0.1225(2)	0.3308(2)	3.1(2)					

Table 3 Interatomic bond distances (Å) and angles (°) for $[Ru_2Cl_5(CO)(PPh_3)_3] \cdot CH_2Cl_2$, for all atoms excluding phenyl rings of PPh_3, which were refined as rigid groups.

(a) Bond distances

Ru(1)	– Cl(1)	2.461(2)	P(1)	– C(111)	1.848(3)
Ru(1)	– Cl(2)	2.482(2)	P(1)	– C(121)	1.840(4)
Ru(1)	– Cl(3)	2.476(2)	P(1)	– C(131)	1.837(4)
Ru(1)	– P(1)	2.366(2)	P(2)	– C(211)	1.839(4)
Ru(1)	– P(2)	2.348(2)	P(2)	– C(221)	1.829(4)
Ru(1)	– C(1)	1.817(6)	P(2)	– C(231)	1.821(5)
Ru(2)	– Cl(1)	2.473(2)	P(3)	– C(311)	1.827(4)
Ru(2)	– Cl(2)	2.443(2)	P(3)	– C(321)	1.824(4)
Ru(2)	– Cl(3)	2.457(2)	P(3)	– C(331)	1.841(5)
Ru(2)	– Cl(4)	2.388(2)	C(1)	– O(1)	1.157(7)
Ru(2)	– Cl(5)	2.407(4)	Cl(6)	– C(2)	1.79(1)
Ru(2)	– P(3)	2.296(2)	Cl(7)	– C(2)	1.70(1)

(b) Bond angles

Cl(1)	– Ru(1)	– Cl(2)	78.57(6)	Ru(1)	– P(2)	– C(211)	117.9(1)
Cl(1)	– Ru(1)	– Cl(3)	81.30(6)	Ru(1)	– P(2)	– C(221)	119.2(2)
Cl(1)	– Ru(1)	– P(1)	87.26(6)	Ru(1)	– P(2)	– C(231)	109.8(2)
Cl(1)	– Ru(1)	– P(2)	170.14(6)	Ru(2)	– P(3)	– C(311)	116.6(2)
Cl(1)	– Ru(1)	– C(1)	94.7(2)	Ru(2)	– P(3)	– C(321)	116.1(2)
Cl(2)	– Ru(1)	– Cl(3)	78.38(6)	Ru(2)	– P(3)	– C(331)	114.6(2)
Cl(2)	– Ru(1)	– P(1)	165.75(6)	Ru(1)	– C(1)	– O(1)	174.5(5)
Cl(2)	– Ru(1)	– P(2)	92.83(6)	C(111)	– P(1)	– C(121)	100.6(2)
Cl(2)	– Ru(1)	– C(1)	90.1(2)	C(111)	– P(1)	– C(131)	100.2(2)
Cl(3)	– Ru(1)	– P(1)	98.09(6)	C(121)	– P(1)	– C(131)	104.7(2)
Cl(3)	– Ru(1)	– P(2)	92.32(6)	C(211)	– P(2)	– C(221)	101.9(2)
Cl(3)	– Ru(1)	– C(1)	168.3(2)	C(211)	– P(2)	– C(231)	102.5(2)
P(1)	– Ru(1)	– P(2)	101.14(6)	C(221)	– P(2)	– C(231)	103.5(2)
P(1)	– Ru(1)	– C(1)	92.7(2)	C(311)	– P(3)	– C(321)	103.5(2)
P(2)	– Ru(1)	– C(1)	90.1(2)	C(311)	– P(3)	– C(331)	101.3(2)
Cl(1)	– Ru(2)	– Cl(2)	79.07(6)	C(321)	– P(3)	– C(331)	102.6(2)
Cl(1)	– Ru(2)	– Cl(3)	81.45(6)	Cl(6)	– C(2)	– Cl(7)	109.8(7)
Cl(1)	– Ru(2)	– Cl(4)	88.78(6)	P(1)	– C(111)	– C(112)	122.0(2)
Cl(1)	– Ru(2)	– Cl(5)	91.65(8)	P(1)	– C(111)	– C(116)	117.8(2)
Cl(1)	– Ru(2)	– P(3)	179.24(6)	P(1)	– C(121)	– C(122)	120.6(3)
Cl(2)	– Ru(2)	– Cl(3)	79.48(6)	P(1)	– C(121)	– C(126)	119.4(3)
Cl(2)	– Ru(2)	– Cl(4)	164.76(6)	P(1)	– C(131)	– C(132)	116.8(3)
Cl(2)	– Ru(2)	– Cl(5)	90.77(8)	P(1)	– C(131)	– C(136)	123.1(3)
Cl(2)	– Ru(2)	– P(3)	101.52(6)	P(2)	– C(211)	– C(212)	119.3(3)
Cl(3)	– Ru(2)	– Cl(4)	89.71(6)	P(2)	– C(211)	– C(216)	120.4(3)
Cl(3)	– Ru(2)	– Cl(5)	168.94(8)	P(2)	– C(221)	– C(222)	119.3(3)
Cl(3)	– Ru(2)	– P(3)	99.12(6)	P(2)	– C(221)	– C(226)	120.7(3)
Cl(4)	– Ru(2)	– Cl(5)	98.82(8)	P(2)	– C(231)	– C(232)	119.4(3)
Cl(4)	– Ru(2)	– P(3)	90.72(6)	P(2)	– C(231)	– C(236)	120.7(3)
Cl(5)	– Ru(2)	– P(3)	87.87(8)	P(3)	– C(311)	– C(312)	116.5(3)
Ru(1)	– Cl(1)	– Ru(2)	84.46(6)	P(3)	– C(311)	– C(316)	122.9(3)
Ru(1)	– Cl(2)	– Ru(2)	84.64(6)	P(3)	– C(321)	– C(322)	121.6(3)
Ru(1)	– Cl(3)	– Ru(2)	84.47(6)	P(3)	– C(321)	– C(326)	118.5(3)
Ru(1)	– P(1)	– C(111)	113.1(1)	P(3)	– C(331)	– C(332)	119.9(3)
Ru(1)	– P(1)	– C(121)	121.0(1)	P(3)	– C(331)	– C(336)	120.1(3)
Ru(1)	– P(1)	– C(131)	114.4(1)				

The EPR spectrum was obtained from a polycrystalline powder sample, using a quartz tube, on a Varian E-109 spectrometer equipped with a Q-band bridge at liquid nitrogen temperature (77 K). Conditions are described in Figure 3.

Cyclic voltammetry

The cyclic voltammogram was recorded at 25.0 ± 0.1 °C in freshly distilled dichloromethane with 0.1 M tetrabutylammonium perchlorate (TBAP) using an EG and PAR electrochemical system with a 175 Universal Programmer. A three electrode system consisting of platinum working and auxiliary electrodes and a reference electrode (Ag/AgCl) with a Luggin-Haber containing salt bridge, filled with the solvent and supporting electrolyte (TBPA) was employed. The ferrocenium(Fc^+)/ferrocene(Fc) couple, at 0.50 V, was employed as reference.

Elemental analysis

Microanalysis was performed on crystalline samples (Microanalyses Laboratory of the Universidade de São Paulo – Instituto de Química).

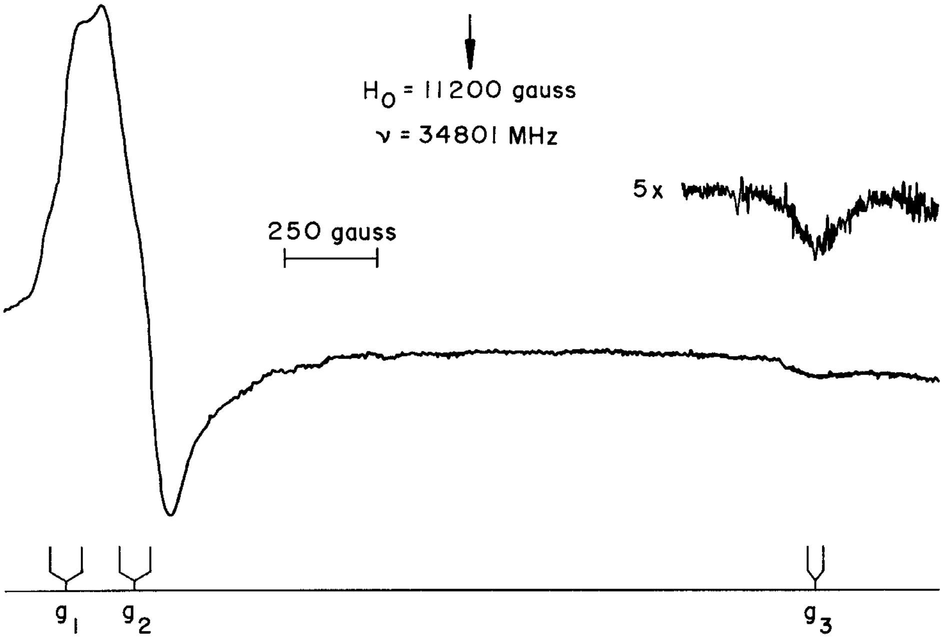

Figure 3 EPR spectrum of the binuclear complex $[Ru_2Cl_5(CO)(PPh_3)_3] \cdot CH_2Cl_2$ measured at 77 K. The stick diagram shows the hyperfine splitting in the low field region due to the phosphorous nuclear spin ($I = 1/2$) interaction. The splitting of g_3 was obtained with 5 G field modulation and 12 db microwave power.

Electrical conductivity

Solution electrical conductivities were measured at 25°C under anaerobic conditions using a Micronal B-330 conductivity bridge with platinum electrodes.

^1H NMR spectrum

This was measured in CD_2Cl_2 on a Bruker AC-200 spectrophotometer.

RESULTS AND DISCUSSION

The IR spectrum of the yellow solid obtained in the initial step of the synthesis shows a strong ν_{CO} stretch at 1997 cm^{-1} and a band at 1600 cm^{-1} assigned to coordinated DMA. This observation, together with the microanalysis of this solid which confirms the presence of nitrogen in the sample, suggests that during the reaction part of the starting material was reduced to $[RuCl_2(CO)_2(PPh_3)_2]$ (which shows the ν_{CO} band near 1997 cm^{-1} [7,15]) and during the subsequent recrystallization process the following reaction occurs,

$$RuCl_2(CO)_2(PPh_3)_2 + RuCl_3(PPh_3)_2DMA \rightarrow Ru_2Cl_5(CO)(PPh_3)_3 + PPh_3 + DMA + CO \qquad (1)$$

producing the insoluble mixed-valence complex containing three bridging chloride ligands. This reaction pathway is consistent with the easy dissociation of the carbon monoxide ligand from $[RuCl_2(CO)_2(PPh_3)_2]$[15,16] and is further supported by the ^1H NMR spectrum of free triphenylphosphine, isolated from the filtrate after removal of the red-brown crystals. To confirm the above mechanism of formation of the bridged compound, reaction (*1*) was reproduced from the previously purified reagents: pure *ttt*-isomer $[RuCl_2(CO)_2(PPh_3)_2]$ was added to $[RuCl_3(PPh_3)_2DMA]\cdot DMA$ previously dissolved in CH_2Cl_2 (*ca* 1:1) and to this solution was added ethanol and ether (to reproduce the solution used for recrystallisation described in the experimental part). After one night the red crystals formed were collected and characterized by IR and microanalysis (carbon and hydrogen) which indicated the same compound as that obtained through the direct reaction of $[RuCl_3(PPh_3)_2DMA]\cdot DMA$ with carbon monoxide, followed by recrystallization.

X-ray diffaction studies showed that the $[Ru_2Cl_5(CO)(PPh_3)_3]$ complex crystallizes as a dichloromethane solvate, consisting of two ruthenium centres with distorted octahedral coordination and with an asymmetric configuration, joined through three bridging chloride atoms. Figure 2 is a schematic drawing of the complex showing the labelling of several non-H atoms. Reported ruthenium(II)-phosphorus distances typically span the range 2.32–2.44Å, depending on the σ or π acidity of the *trans* ligand.[17,18] The Ru(1)-P(1) and Ru(1)-P(2) bond distances, both *trans* to bridge chlorides, are 2.366(2) and 2.348(2)Å, respectively. The shorter distance found for Ru(2)-P(3) [2.296(2)Å], which is also *trans* to a bridge chloride, suggests that the Ru(2) centre is a Ru^{III} ion, whereas the Ru(1) is probably Ru^{II}. The bridging chlorides that are *trans* to triphenylphosphine and carbon monoxide ligands show slightly longer Ru-Cl distances [2.461(2)Å, 2.473(2)Å, 2.476(2) and 2.482(2)Å] when compared to those of the bridging chlorides that are *trans* to the non-bridging chloride atoms [2.443(2)Å and 2.457(2)Å]. This effect is probably due to the weaker *trans* influence of the chloro ligands when compared with triphenylphosphine and carbon monoxide ligands. The Ru-P and Ru-Cl bondlengths and Ru-μCl-Ru angles are comparable to those found in other reported binuclear bridged ruthenium complexes.[19,20,21,22] In our complex the Ru-Cl-Ru bridging angle is on average 84.5° and hence the ruthenium atoms are further apart than they would be in a regular cofacial bioctahedron (two regular octaedra sharing one face have a bridging angle $\alpha = 70.5°$ [19]) and the distance between the ruthenium centres found here [3.315(6)Å] is significantly longer than the distance of 3.115Å in $Ru_2Cl_5[P(n\text{-}C_4H_9)_3]_4$[20] and 3.251(1)Å in $Ru_2Cl_5(chiraphos)_2$,[6] and well outside the range 2.28–2.95Å usually found for a Ru-Ru bond.[23,24,25]

The infrared spectrum of the title complex shows, in the carbonyl region, only one band at 1964 cm^{-1} corresponding to the CO stretch. The shift of the ν_{CO} band towards lower frequencies has been reported for a variety of Ru(II) species[15,22,26] and indicates strong metal-CO back bonding.[27] The IR spectrum also shows bands at 328 and 280 cm^{-1}, characteristic of terminal chlorides, and bands at 250 and 225 cm^{-1} which can be associated with the streching of the chloro-bridge ligands.[7] Characteristic vibrations of P-C (aromatic) stretching are observed at 746, 696 and 518 cm^{-1}.[28,29]

The presence of both Ru^{II} and Ru^{III} species in the present binuclear complex is confirmed by the EPR spectrum measured at 35 GHz (Figure 3), which is characteristic of a magnetically isolated Ru^{III} ion. The EPR signal must be completely different in the case of an intermetallic interaction with consequent delocalization of the unpaired electron over the two Ru ions. On the other hand, for a hypothesis of both ions being Ru^{III}, spin-spin coupling would be expected to give again a different signal or even no signal due to antiferromagnetic coupling. By simulation of the powder spectrum data the three g-tensor values were calculated ($g_1 = 2.4600$, $g_2 = 2.4120$, $g_3 = 2.0485$). The difference between g_1 and g_2 suggests a small rhombic distortion around the Ru^{III} centre, compatible with the X-ray structure. The splitting observed in the low field region of the spectrum indicates a hyperfine interaction due to the presence of one phosphorus (nuclear spin 1/2). The hyperfine A-tensor was calculated as $A_1 = 81.4$ G; $A_2 = 88.9$ G; $A_3 = 35.0$ G, showing that the Ru^{III} species is effectively coordinated to a single phosphorus atom.

In $CDCl_3$, the electronic spectrum of the complex shows three bands: 287 nm ($\varepsilon = 688\ M^{-1}\ cm^{-1}$), 401 nm ($\varepsilon = 261\ M^{-1}\ cm^{-1}$) and 481 nm ($\varepsilon = 165\ M^{-1}\ cm^{-1}$). The complexes $[(PPh_3)_2CORuCl_3RuCl(PPh_3)_2]^+$, $[(PPh_3)_2CSRuCl_3RuCl(PPh_3)_2]^+$ and $[(Ptol_3)_2CORuCl_3RuCl(Ptol_3)_2]^+$ which have intervalence charge transfer bands at 675 nm (ε *ca* 100 $M^{-1}\ cm^{-1}$) exhibit a small degree of delocalisation.[30] This was attributed to the influence of π-acid ligands like CO and CS which reduce the tendency to delocalisation of charges and when asymmetrically located, these ligands shift the transition to higher energies.[30] It is therefore possible to suggest that one of the bands present in the spectrum of our complex, probably the one at 481 nm, can be assigned to an intervalence charge transfer. The spectroscopic characteristics of the present complex suggest it to be of Class I type, within the classification of Robin and Day,[31] with completely localized charges.

A millimolar solution of the title complex was prepared in deoxygenated CH_2Cl_2 and the conductivity data indicated that the diruthenium complex is not an electrolyte (1.0×10^{-3} M; $\Omega_M = 0.03\ Scm^2\ mol^{-1}$). Electrochemical studies of the complex show two redox processes corresponding to the reduction of the compound to $[Ru_2Cl_5(CO)(PPh_3)_3]^-$ and its oxidation to $[Ru_2Cl_5(CO)(PPh_3)_3]^+$. These results suggest that the "soft" Ru^{II} is oxidized in a high anodic region ($E_{1/2} = 1.19$ V) generating a Ru^{III}/Ru^{III} species. Similarly, the Ru^{II} in $[(PEt_2Ph)_3RuCl_3Ru(PEt_2Ph)_3]^{2+}$ complex is oxidized at the same potential.[30] The inequivalence of intensities of the redox couple in this process (Figure 4) also indicates that the triphenylphosphine ligand coordinated to the metal is oxidized near to the oxidation potential of the Ru^{II} centre. Free triphenylphosphine is irreversiblely oxidized at 0.78 V.[32] The reversible reduction observed at $E_{1/2} = -0.29$ V (II,II ← II,III) for the species synthesized in this work is much smaller than the isomer form shown in Figure 1 ($E_{1/2} = 0.03$ V). This is in accordance to the fact that the chloride ions stabilize better the Ru^{III} system than π-acceptor ligands.

Acknowledgements

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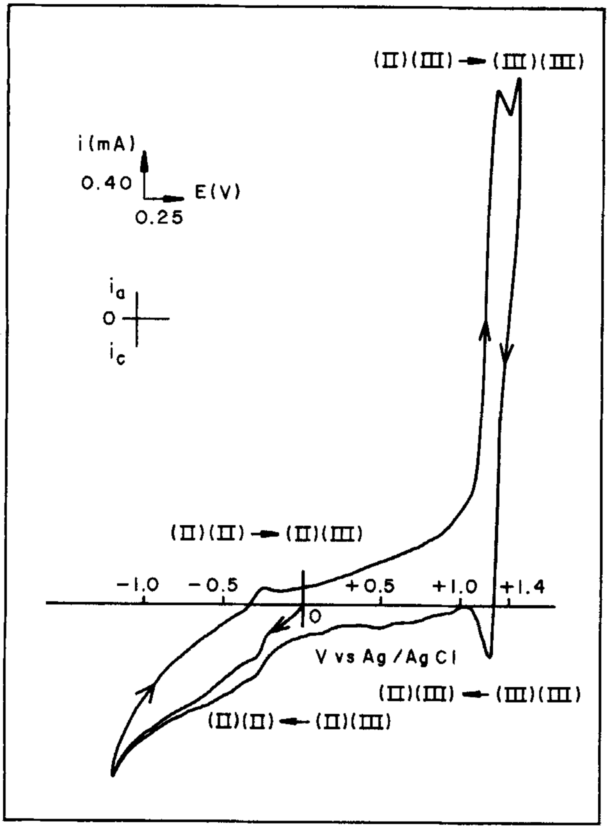

Figure 4 Cyclic voltammogram of $[Ru_2Cl_5(CO)(PPh_3)_3]\cdot CH_2Cl_2$ (scan speed 10 mV s^{-1}).

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