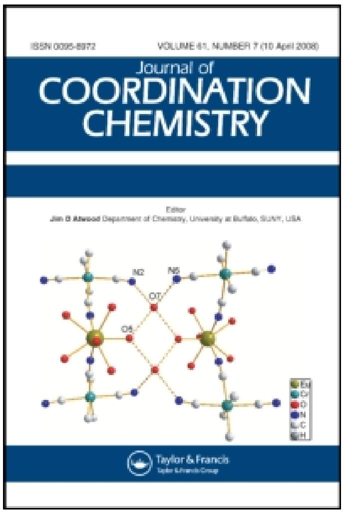

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A SIMPLE ROUTE FOR SYNTHESES OF TRIHALIDE-BRIDGED CARBONYL DIRUTHENIUM(II,III) COMPLEXES: CRYSTAL AND MOLECULAR STRUCTURE OF *ttt*-$[Ru^{II}Cl_2(CO)_2(PPh_3)_2]$,$[(CO)(AsPh_3)_2Ru^{II}(\mu\text{-}Cl_3)Ru^{III}Cl_2(AsPh_3)]$ AND $([CO)(PPh_3)_2Ru^{II}(\mu\text{-}Br_3)Ru^{III}Br_2(PPh_3)]$, SPECTROSCOPIES, ELECTROCHEMISTRY AND PROPERTIES

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A SIMPLE ROUTE FOR SYNTHESES OF TRIHALIDE-BRIDGED CARBONYL DIRUTHENIUM(II,III) COMPLEXES: CRYSTAL AND MOLECULAR STRUCTURE OF *ttt*-$[Ru^{II}Cl_2(CO)_2(PPh_3)_2]$, $[(CO)(AsPh_3)_2Ru^{II}(\mu\text{-}Cl_3)Ru^{III}Cl_2(AsPh_3)]$ AND $[(CO)(PPh_3)_2Ru^{II}(\mu\text{-}Br_3)Ru^{III}Br_2(PPh_3)]$, SPECTROSCOPIES, ELECTROCHEMISTRY AND PROPERTIES

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The triply halide-bridged binuclear complexes $[Ru_2Cl_5(CO)(AsPh_3)_3]$ ($AsPh_3$ = triphenylarsine), $[Ru_2Cl_5(CO)(PPh_3)_2(AsPh_3)]$ (PPh_3 = triphenylphosphine), $[Ru_2Cl_5(CO)(AsPh_3)_2(PPh_3)]$, $[Ru_2Br_5(CO)(PPh_3)_3]$, $[Ru_2Cl_5(CO)(P\{p\text{-}tol\}_3)_2(PPh_3)]$ ($P\{p\text{-}tol\}_3$ = tri-p-tolylphosphine) and $[Ru_2Br_2Cl_3(PPh_3)_2(AsPh_3)]$ were prepared from the precursor compounds *ttt*-$[RuX_2(CO)_2(P)_2]$ (X = Cl or Br) and $[RuY_3(P')_2S]\cdot S$ (Y = Cl or Br; P = PPh_3, $AsPh_3$ or $P\{p\text{-}tol\}_3$ and P′ = $AsPh_3$ or PPh_3; S = DMA or MeOH, where DMA = N,N′-dimethylacetamide). The molecular structures of the binuclear complexes $[Ru_2Cl_5(CO)(AsPh_3)_3]$ ($P2_{1/c}$), $[Ru_2Br_5(CO)(PPh_3)_3]$ ($P2_{1/c}$) and *ttt*-$[RuCl_2(CO)_2(PPh_3)_2]$ ($P\bar{1}$) were determined by X-ray diffraction methods. The complexes are always formed by two Ru atoms bridged through three halide anions, two of which are X type (from the Ru^{II} precursor) and the other is Y type (from the ruthenium^{III} precursor) confirming our previously suggested mechanism for obtaining this class of complexes. The Ru^{II} atom is also coordinated to a carbon monoxide molecule and two P ligands from the *ttt*-starting isomer whereas the Ru^{III} atom is bonded to two non-bridging Y halides and one P′ molecule. The presence of Ru^{III} was confirmed by EPR data, a technique that

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was also useful to suggest the symmetry of the complexes. The absence of intervalence charge-transfer transitions (IT) in the near infrared spectrum confirms that the binuclear complexes have localized valence. The IR spectra of the complexes show ν(CO) bands close to 1970 cm^{-1} and ν(Ru-Cl) or ν(Ru-Br) bands at about 230–380 cm^{-1} corresponding to halides at terminal or bridged positions. Two widely separated redox processes, $Ru^{II}/Ru^{II} \leftarrow Ru^{II}/Ru^{III} \rightarrow Ru^{III}/Ru^{III}$, were observed by cyclic voltammetry and differential pulse voltammetry.

Keywords: Binuclear ruthenium (II,III) complexes; Dicarbonyl complex; Phosphines and arsine; X-ray structure; Spectroscopical measurements; Electrochemistry

INTRODUCTION

Syntheses and studies of dinuclear ruthenium phosphine complexes with formal oxidation states (II, III) are not new in the literature. Over 30 years ago Nicholson reported the synthesis of the dark red $Ru_2Cl_5(PBu_3)_4$(1) complex from the reaction of ruthenium(III) chloride with tri-n-butyl-phosphine (PBu_3) [1]. The X-ray crystallography of this compound demonstrated that its structure is a face-sharing bioctahedral [2]. More recently a green structural isomer of (1) was obtained as a by-product from basically the same reaction reported previously by Nicholson, except that in this case the reaction mixture was exposed longer to air [3]. Several others isomers of the type $[Ru_2Cl_5L_4]$ ($L = AsPh_3$, $As(p\text{-tol})_3$, $As\text{-}(p\text{-PhCl})_3$, PEt_2Ph, PMe_2Ph; $L_2 = Ph_2As(CH_2)_2\,AsPh_2$) were obtained [4]. Dinuclear ruthenium (II, III) complexes with biphosphines of general formula $[Ru_2Cl_5(P\text{-}P)_2]$ were also synthesized and characterized [5, 6]. A few years ago, we developed in our laboratory a simple method to synthesize $[(CO)(PPh_3)_2\,Ru(\mu\text{-}Cl_3)RuCl_2(PPh_3)]$ as a new type of carbonyl-ruthenium (II, III) complex [7]. In this paper, we confirm the efficiency of our methodology for other carbonyl mixed valence complexes using different ligands. One of the main contributions of this paper is to extend our methodology to obtain mixed valence ruthenium complexes containing different halide-bridges (*i.e.*, Cl^- and Br^-) and different coordinating ligands including the fully pentabromo complex.

EXPERIMENTAL

X-ray Crystallographic Analyses of *ttt*-$[RuCl_2(CO)_2(PPh_3)_2]$, $[Ru_2Cl_5(CO)(AsPh_3)_3]$ and $[Ru_2Br_5(CO)(PPh_3)_3]$

Crystallographic data for the three complexes are summarized in Table I. The final-cell parameters were obtained by least squares on the setting angles for 25 reflections with typical ranges of 2θ. Data were corrected for

TABLE I Crystal data, data collection details and structure refinement results for *ttt*-[$RuCl_2(CO)_2(PPh_3)_2$](1), [$Ru_2Cl_5(CO)(AsPh_3)_3$](2) and [$Ru_2Br_5(CO)(PPh_3)_3$] CH_2Cl_2(3)

Complexes	1	2	3
formula	$C_{38}Cl_2H_{30}O_2P_2Ru$	$C_{55}Cl_5H_{45}OAs_3Ru_2$	$C_{56}Br_5Cl_2H_{47}OP_3Ru_2$
Mol wt	752.53	1326.06	1501.44
System	Triclinic	Monoclinic	Monoclinic
Space group	P1	$P2_1/c$	$P2_1/c$
Lattice parameters			
A	9.0866(1) Å	14.739(1) Å	14.8044(1) Å
B	10.3456(1) Å	18.027(1) Å	18.542(2) Å
C	11.003(5) Å	20.492(1) Å	20.599(9) Å
α	108.29(2)°	90.00(1)°	90.000(18)°
β	113.67(2)°	100.12(1)°	100.66(2)°
γ	100.073(5)°	90.00(1)°	90.000(8)°
V	843.87 $Å^3$	5360(5) $Å^3$	5557(3) $Å^3$
Z	1	4	4
D_c	1.481 $g.cm^{-3}$	1.643 $g.cm^{-3}$	1.795 $g.cm^{-3}$
Crystal dimensions	0.2 × 0.2 × 0.05 mm	0.03 × 0.09 × 0.45 mm	0.1 × 0.1 × 0.1 mm
Radiation MoKα	$\lambda = 0.70930$ Å	$\lambda = 0.71073$ Å	$\lambda = 0.71073$ Å
T	25°C	25°C	25°C
Scan technique	ω-2θ	ω-2θ	ω-2θ
Scan speed range	6.7–20 (°min^{-1})	6.7–20 (°min^{-1})	6.7–20 (°min^{-1})
θ range for data collect	0–25°	0–22°	0–65°
No. Ind. Reflns	3807	5239	9443
No. Reflns [$I > 3\sigma(I)$]	2979	2739	9153
No. Refined parameters	206	421	514
Minimized function	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Weighting scheme	$w = [\sigma^2(\lvert F_o\rvert) + 0.001\lvert F_c\rvert^2]$	$w = [\sigma^2(\lvert F_o\rvert) + 0.001\lvert F_c\rvert^2]$	$w = [\sigma^2(\lvert F_o\rvert) + 0.001\lvert F_c\rvert^2]$
$R = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$	0.0343	0.068	0.04830
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.0576	0.068	0.0523
h_{min}, h_{max}; k_{min}, k_{max}; l_{min}, l_{max}	−10, 9; −12, 11; 0, 13	0, 15; 0, 19; −21, 21	17, −17; 0, 21; 0, 23
Max.; min. Residual ρ	−0.5–0.49(e. $Å^{-3}$)	−1.24–1.00 (e. $Å^{-3}$)	2.728; −2.759(e. $Å^{-3}$)

Lorentz and polarization effects, and absorption, using the method of Walker and Stuart [8]. The intensities of standard reflections were essentially constant throughout the experiments. The structures were solved using Patterson methods and difference Fourier techniques. All hydrogen atoms were included as fixed contributors, with a common isotropic temperature factor $B = 4.6\,\text{Å}^2$. Scattering factors for non-hydrogen atoms were taken from Cromer and Mann [9], with corrections for anomalous dispersion from Cromer and Liberman [10], and for hydrogen atoms from Stewart *et al.* [11]. The programs used were: SHELX97 [12] and ORTEP [13].

Reagents and Instruments

The 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 dioxygen.

Infrared spectra were recorded as CsI pellets on a Bomen-Michelson 102 instrument. The UV-Vis spectra in CH_2Cl_2 were recorded on a HP 8452A spectrophotometer and are given as λ_{max}(nm) (log ε, in $M^{-1}cm^{-1}$), sh = shoulder. EPR spectra were measured at −160°C using a Varian E-109 Instrument operating at the X band frequency, within a rectangular cavity (E-248) fitted with a temperature controller.

Cyclic and differential pulse voltammetries were carried out at room temperature in freshly distilled dichlorometane containing 0.1 m of Bu_4N^+ ClO_4^-(TBAP), using an EG&G/PARC electrochemical system consisting of a 273A potentiostat or BAS 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 m TBAP in CH_2Cl_2, a medium in which ferrocene is oxidized at 0.43 V (Fc^+/Fc); all potentials are referred to this electrode.

Elemental analyses were performed at the Institute of Chemistry of the University of São Paulo, São Paulo or at the Department of Chemistry of the Federal University of São Carlos, São Carlos.

Syntheses

All complexes, $RuBr_3$ [14], $[RuCl_3(PPh_3)_2DMA]\cdot DMA$, $[RuBr_3(PPh_3)_2DMA]\cdot DMA$, $RuCl_3(P\{p\text{-tol}\}_3)_2DMA]\cdot DMA$, $[RuBr_3(PPh_3)_2DMA]\cdot$

DMA, $[RuCl_3(AsPh_3)_2MeOH]\cdot MeOH$ [15, 16], *ttt*-$[RuCl_2(CO)_2(PPh_3)_2]$, *ttt*-$[RuCl_2(CO)_2(P\{p\text{-}tol\}_3)_2]$; *ttt*-$[RuCl_2(CO)_2(AsPh_3)_2]$ and *ttt*-$[RuBr_2(CO)_2(PPh_3)_2]$ [17] were prepared by literature methods.

Binuclear synthesis: These complexes were each prepared from the corresponding carbonyl {*ttt*-$[RuX_2(CO)_2(P)_2]$} ($X = Br$ or Cl) and the solvated complexes $[RuY_3(P')_2S]\cdot S$ ($Y = Br$ or Cl) ($P = PPh_3$, $AsPh_3$ or $P\{p\text{-}tol\}_3$ and $P' = PPh_3$, $AsPh_3$; $S = DMA$ or MeOH). The complexes were dissolved in dichloromethane (10 mL) in a 1:1 ratio and ethyl ether (~3 mL) was added. Crystals were deposited from the solutions in the Schlenk flasks within about 3 days. In the case of the bromo-only complex, the product of the small-scale reaction was characterized completely by single crystal X-ray.

$[Ru_2Cl_5(CO)(AsPh_3)_3]$ (Yield: 0.063 g; 45%) – *ttt*-$[RuCl_2(CO)_2(AsPh_3)_2]$ (0.089 g - 0.10 mmol) $[RuCl_3(AsPh_3)_2MeOH]\cdot MeOH$ (0.093 g - 0.10 mmol) Anal. Calcd. for $Ru_2Cl_5C_{55}H_{45}As_3O$%: C, 49.81; H, 3.42. Found: C, 50.05; H, 3.49.

$[Ru_2Cl_5(CO)(AsPh_3)_2(PPh_3)]$ (Yield: 0.061 g; 40 %) – *ttt*- $[RuCl_2(CO)_2(AsPh_3)_2]$ (0.100 g - 0.12 mmol) $[RuCl_3(PPh_3)_2DMA]\cdot DMA$ (0.108 g - 0.12 mmol) Anal. Calcd. for $Ru_2Cl_5C_{55}H_{45}As_2PO$: C, 51.52; H, 3.54%. Found: C, 51.75; H, 3.63%.

$[Ru_2Cl_5(CO)(PPh_3)_2(AsPh_3)]$ (0.066 g; 42%) – *ttt*-$[RuCl_2(CO)_2(PPh_3)_2]$ (0.096 g - 0.13 mmol) $[RuCl_3(AsPh_3)_2MeOH]\cdot MeOH$ (0.113 g - 0.13 mmol) Anal. Calcd. for $Ru_2Cl_5C_{55}H_{45}P_2AsO$%: C, 53.35; H, 3.66. Found: C, 52.98; H, 3.67.

$[Ru_2Cl_5(CO)(P\{p\text{-}tol\}_3)_2(PPh_3)]$ (Yield: 0.061 g; 45%) – *ttt*-$[RuCl_2(CO)_2\{P(p\text{-}tol)_3\}_2]$ (0.089 g - 0.11 mmol) $[RuCl_3(PPh_3)_2DMA]\cdot DMA$ (0.096 g - 0.11 mmol) Anal. Calcd. for $Ru_2Cl_5C_{61}H_{57}P_3O$%: C, 57.31; H, 4.49. Found: C, 57.41; H, 4.75.

$[Ru_2Br_2Cl_3(CO)(PPh_3)_2(AsPh_3)]$ (Yield: 0,063 g; 39%) – *ttt*-$[RuBr_2(CO)_2\{PPh_3\}_2]$ (0.102 g - 0.12 mmol) $[RuCl_3(AsPh_3)_2MeOH]\cdot MeOH$ (0.107 g - 0.12 mmol) Anal. Calcd. for $Ru_2Br_2Cl_3C_{55}H_{45}P_2AsO$%: C, 49.78; 3.42. Found: C, 50.21; H, 3.40.

$[Ru_2Br_5(CO)(PPh_3)_3]$ - $[RuBr_2(CO)_2(PPh_3)_2]$ (0.050 g - 0.06 mmol) $[RuBr_3(PPh_3)_2DMA]\cdot DMA$ (0.062 g - 0.06 mmol).

RESULTS AND DISCUSSION

Molecular Structures

The molecular structure of *ttt*-$[RuCl_2(CO)_2(PPh_3)_2]$, one of the starting materials for syntheses in this work, shows the Cl atoms to be *trans* (Fig. 1).

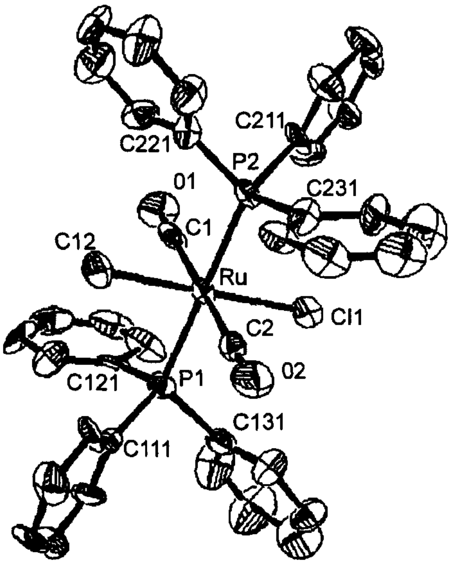

FIGURE 1 Ortep drawing of the *ttt*-$[RuCl_2(CO)_2(PPh_3)_2]$.

The geometry of the Ru is distorted octahedral, with the Ru—Cl, Ru—C and Ru—P bond lengths 2.407(1), 1.995(4) and 2.410(1) Å, respectively. The Ru—Cl and Ru—P distances are within the well-established range for Ru(II) complexes [19]. The Ru—C distances for the *ttt*-$[RuCl_2(CO)_2(PPh_3)_2]$ complex, 1.995(4) Å, are longer than the equivalent bond length for the *cct*-$[RuCl_2(CO)_2(PPh_3)_2]$, where the *cis*(CO) is *trans* to Cl in this complex (av. 1.859(4) Å) [20], or for the *cis*-isomer of $[RuCl_2(CO)_2(BzI_3P)_2]$ where Ru—C is *ca.* 1.863 Å [21].

The *trans*(CO) isomer of this latter complex shows a Ru—C bond length close to that found for our complex (1.948 Å) [21]. This observation has been explained by the stronger *trans* influence of carbon monoxide when compared with chloride [22]. The C—O bond length for *ttt*-$[RuCl_2(CO)_2(PPh_3)_2]$ is 1.028(5) Å, shorter than the distance for its *cis*-isomer where the distance C—O is 1.130(5) Å (av) [20]. This is probably a consequence of the cooperative effect present in the *cis*-CO species.

In the complex $[Ru_2Cl_5(CO)(AsPh_3)_3]$ the bond length of Ru(1)—C(1) and C(1)—O are 1.76(3) and 1.20(3) Å, respectively. The significantly shorter Ru—C distance for this complex, compared with the *cct*-$[RuCl_2(CO)_2(AsPh_3)_2]$ [20], with Ru—C [1.873(5) and 1.848(5) Å] and C—O [1.112(6) and 1.142(6) Å], suggests that the bridged-chloride exhibits a weaker *trans* influence than the terminal chloride.

For $[RuCl_2(CO)(1\text{-methylpyridine})(PPh_3)_2]$ [23], where the CO is *trans* to the 1-methylpyridine ligand, the Ru—C distance is 2.02(1) Å confirming the small *trans* influence of the bridged chloride in the $[Ru_2Cl_5(CO)(AsPh_3)_3]$ complex. For $[Ru_2Br_5(CO)(PPh_3)_3]$ these distances are 1.831 and 1.144 Å, respectively. The Ru–Ru distance for the bromine complex (3.455 Å) is longer as expected, than the same distances for $[Ru_2Cl_5(CO)(PPh_3)_3]$ (3.315 Å) [7] and $[Ru_2Cl_5(CO)(AsPh_3)_3]$ (3.246(3) Å).

Cotton and Torralba [3] have characterized a series of Ru(II, III) complexes with face-sharing bioctahedra of the general formula $[Ru_2Cl_5(PR_3)_4]$ and found Ru–Ru distances of 3.279(2) Å for the $[(PBu_3)_3Ru(\mu\text{-}Cl_3)RuCl_2PBu_3]$, 2.994(0) Å for the $[(PMe_2Ph)_2ClRu(\mu\text{-}Cl_3)RuCl(PMe_2Ph)_2]$ and 2.992(1) Å for the $[(PMe_3)_2ClRu(\mu\text{-}Cl_3)RuCl(PMe_3)_2]$. These authors have demonstrated that longer Ru–Ru distances for $Ru^{II}-Ru^{III}$ complexes (2.99–3.28 Å) result in enlarged Ru–Cl_b–Ru angles (75.1–83.6°) and contracted Cl–Ru–Cl_b (80.4–86.2°), where Cl_b is a bridging chloride. As can be seen in Table III these angles are within the suggested ranges [3] including the bromine complex.

The question of whether a Ru–Ru bond exists in some mixed valence compounds can be answered if we compare the distances between the metal centers and their face-sharing bioctahedral angles. Thus for the $[Ru_2Br_3(NH_3)_6]^{2+}$ the Ru–Ru distance is 2.852(4) Å and the angle Ru-Br-Ru is 68°, smaller than 70.5° (given by $\cos\theta/2 = 2/3$) which is the angle found for two regular octahedra sharing one face [2]. In this compound, there is, unequivocally, a Ru–Ru bond.

On the other hand, a preliminary survey of the structural data tabulated in Table IV shows that our complexes are similar to those in the literature

TABLE II Selected bond distances (Å) for *ttt*-$[RuCl_2(CO)_2(PPh_3)_2]$, $[Ru_2Br_5(CO)(PPh_3)_3]$ and $[Ru_2Cl_5(CO)(AsPh_3)_3]$

ttt-$[RuCl_2(CO)_2(PPh_3)_2]$			$[Ru_2Br_5(CO)(PPh_3)_3]$			$[Ru_2Cl_5(CO)(AsPh_3)_3]$		
Ru	Cl(1)	2.407(1)	Ru(1)	Ru(2)	3.445(8)	Ru(1)	Ru(2)	3.246(3)
Ru	C(1)	1.995(4)	Ru(1)	Br(1)	2.5846(1)	Ru(1)	Cl(11)	2.460(6)
Ru	P(1)	2.410(1)	Ru(1)	Br(2)	2.6175(1)	Ru(1)	Cl(12)	2.438(6)
C(1)	O(1)	1.028(5)	Ru(1)	Br(3)	2.6128(1)	Ru(1)	Cl(13)	2.415(6)
P(1)	C(111)	1.834(4)	Ru(1)	C(1)	1.831(9)	Ru(1)	As(1)	2.443(3)
P(1)	C(121)	1.821(5)	Ru(1)	P(1)	2.357(2)	Ru(1)	As(2)	2.425(3)
P(1)	C(131)	1.831(4)	Ru(1)	P(2)	2.376(2)	Ru(1)	C(1)	1.76(3)
			Ru(2)	Br(1)	2.5996(1)	Ru(2)	Cl(11)	2.441(6)
			Ru(2)	Br(2)	2.5626(1)	Ru(2)	Cl(12)	2.442(6)
			Ru(2)	Br(3)	2.5587(1)	Ru(2)	Cl(13)	2.445(6)
			Ru(2)	Br(4)	2.4666(1)	Ru(2)	Cl(21)	2.342(6)
			Ru(2)	Br(5)	2.4670(1)	Ru(2)	Cl(22)	2.33(1)
			C(1)	O(1)	1.144(2)	Ru(2)	As(3)	2.392(3)

TABLE III Selected bond angles (°) for *ttt*-[$RuCl_2(CO)_2(PPh_3)_2$], [$Ru_2Br_5(CO)(PPh_3)_3$] and [$Ru_2Cl_5(CO)(AsPh_3)_3$]

ttt-[$RuCl_2(CO)_2(PPh_3)_2$]				[$Ru_2Br_5(CO)(PPh_3)_3$]				[$Ru_2Cl_5(CO)(AsPh_3)_3$]			
Cl(1)	Ru	C(1)	93.1(1)	Br(1)	Ru(1)	Br(3)	82.66(3)	Cl(11)	Ru(1)	Cl(12)	79.7(2)
Cl(1)	Ru	P(1)	89.76(3)	Br(1)	Ru(1)	Br(2)	78.54(3)	Cl(11)	Ru(1)	Cl(13)	81.9(2)
C(1)	Ru	P(1)	90.7(1)	Br(3)	Ru(1)	Br(2)	77.98(3)	Cl(12)	Ru(1)	Cl(13)	80.5(2)
Ru	C(1)	O(1)	178.6(4)	P(1)	Ru(1)	P(2)	100.47(7)	Cl(11)	Ru(1)	C(1)	171.2(8)
Ru	P(1)	C(111)	119.1(1)	Br(1)	Ru(1)	C(1)	93.7(3)	Cl(12)	Ru(1)	As(1)	166.8(2)
Ru	P(1)	C(121)	111.3(1)	Br(1)	Ru(1)	P(1)	170.91(6)	Cl(12)	Ru(1)	As(2)	92.4(2)
Ru	P(1)	C(131)	116.8(1)	Br(1)	Ru(1)	P(2)	87.51(6)	Cl(11)	Ru(2)	Cl(12)	80.0(2)
				Br(4)	Ru(2)	Br(5)	99.05(5)	Cl(11)	Ru(2)	Cl(13)	81.7(2)
				Br(4)	Ru(2)	Br(3)	89.72(4)	Cl(11)	Ru(2)	Cl(21)	171.2(3)
				Br(5)	Ru(2)	Br(3)	169.50(5)	Cl(11)	Ru(2)	Cl(22)	90.0(3)
				Br(4)	Ru(2)	P(3)	91.39(7)	Cl(12)	Ru(2)	Cl(13)	79.8(2)
				Br(5)	Ru(2)	P(3)	87.92(7)	Cl(12)	Ru(2)	Cl(21)	92.4(2)
				Ru(1)	Br(1)	Ru(2)	83.58(3)	Ru(1)	Cl(11)	Ru(2)	83.0(2)
				Ru(1)	Br(2)	Ru(2)	83.66(3)	Ru(1)	Cl(12)	Ru(2)	83.4(2)
				Ru(1)	Br(3)	Ru(2)	83.83(3)	Ru(1)	Cl(13)	Ru(2)	83.8(2)

TABLE IV Selected structural parameters for face-sharing bioctahedral rutheniumII/III complexes

	Ru−Ru Å	*∠Ru−X$_b$−Ru deg*	*∠X$_b$−Ru−X$_b$ deg*	*Ref.*
$L_2L'RuX_3RuX_2L$				
L = L′ = Pbu$_3$, X = Cl	3.28	83.6	80.4	3
L = L′ = PEt$_2$Ph, X = Cl	3.28	82.9		4
L = L′ = PPh$_3$, X = Cl	3.31			7
L = AsPh$_3$, L′ = CO, X = Cl	3.25	83.4	80.7	this work
L = PPh$_3$, = L′ = CO, X = Br	3.45	83.7	80.9	this work
$L_2ClRuCl_3RuClL_2$				
L = PBu$_3$	3.12	79.4	83.5	2
L = PMe$_2$Ph	2.99	75.1	86.7	3
L-L = chiraphos	3.25	83.4	80.6	5
$L_2ClRuCl_3RuClL_2$				
L = PMe$_3$	2.99	75.6	86.2	3

and the angles suggest little if any attraction between the metal atoms. It could be postulated that there is clean valence trapping in these molecules so that one metal atom is a d^6 Ru^{II} (more neutral set of ligands) and the other is a d^5 Ru^{III} (more anionic set of ligands). In accord with electrochemical and EPR experiments on our complexes, this is favorable to an electrostatic interaction at one end (Ru^{III}) and maximizes $d\pi-p\pi$ back bonding at the other end (Ru^{II}) as detected for other complexes from the literature [3]. It is interesting to point out that in our $[(CO)(AsPh_3)_2Ru^{II}(\mu\text{-}Cl_3)Ru^{III}Cl_2(AsPh_3)]$ and $[(CO)(PPh_3)_2Ru^{II}(\mu\text{-}Br_3)Ru^{III}Br_2(PPh_3)]$ complexes the angles ∠Ru−X$_b$−Ru are practically the same (83.4° and 83.7°, respectively). However, the Ru−Ru distance is a little longer for the bromine complex compared with the same compound with chlorine (3.45 and 3.25 Å, respectively) due the bigger atomic radius of the bromine.

Reactivity of *ttt*-[RuX$_2$(CO)$_2$(P)$_2$] and [RuY$_3$(P′)$_2$S]S to Give Dinuclear-mixed Valence Complexes

The *ttt*-$[RuX_2(CO)_2(P)_2]$ compound has been shown previously to be a useful precursor for the preparation of dinuclear-mixed valence complexes [7]. The equimolar reaction of *ttt*-$[RuX_2(CO)_2(P)_2]$ with the solvate $[RuY_3(P')_2S]S$ generates binuclear complexes with a particular pattern of substitution as confirmed by X-ray studies (see Molecular Structures Section) (Eq. (1)).

$$\begin{aligned} &ttt\text{-}[RuX_2(CO)_2(P)_2] + [RuY_3(P')_2S]\cdot S \\ &\quad \rightarrow [(CO)(P)_2Ru^{II}(\mu - X_2Y)Ru^{III}Y_2(P')] + CO + P' + 2S \end{aligned} \tag{1}$$

The IR and UV/Vis spectroscopic data for the binuclear-carbonyl mixed valence complexes are listed in Table V.

In all these complexes the carbonyl group and two $AsPh_3$ or PPh_3 ligands are coordinated to the Ru(II) center. The carbonyl stretches shown in Table V are close to others found for Ru(II)-phosphines species [14]. Some IR bands in the 390-225 cm^{-1} region are tentatively assigned to ν(Ru-Cl). The spectra in this region are complex but the values are reasonable for the type of complexes studied in this work [14, 15]. The infrared spectra of the complexes show bands that are typical of coordinated phosphine and arsine ligands [15, 16].

The electronic spectral data of the carbonyl complexes listed in Table V show three bands typical for this class of compounds [7]. Triple chloride binuclear carbonyl mixed valence compounds such as $[(CO)(PPh_3)_2Ru^{II}(\mu\text{-}Cl_3)Ru^{III}Cl(PPh_3)_2]^+$, $[(CO)(P\{p\text{-}tol_3)_2Ru^{II}(\mu\text{-}Cl_3)Ru^{III}Cl)(P\{p\text{-}tol_3)_2]^+$ and $[(CO)(PPh_3)_2Ru^{II}(\mu\text{-}Cl_3)Ru^{III}Cl_2(PPh_3)]$ or $[(CS)(PPh_3)_2Ru^{II}(\mu\text{-}Cl_3)Ru^{III}Cl(PPh_3)_2]^+$ exhibit a small degree of delocalization and their intervalence charge transfer bands are in the visible region of the spectrum showing low (*ca.* 100 $M^{-1}cm^{-1}$) extinction coefficients [17]. Thus we suggest that those bands at about 540-600 nm (Tab. V), can be assigned to intervalence charge transfer. The spectroscopic characteristics of these structurally asymmetric carbonyl complexes allow us to classify them as Class I type, within the classification of Robin and Day [18], with totally localized charges which is consistent with the presence of a strong π-acid ligand like CO which, when asymmetrically located, reduce the tendency to delocalize charges. This type of strong π-acceptor ligand shifts the

TABLE V IR and UV/Vis data for binuclear-carbonyl mixed valence complexes

Complexes	$\nu(CO)$* $\nu(Ru-Cl) cm^{-1}$	λ_{max}, $\varepsilon_{(M-1cm-1)}$**
$[(CO)(AsPh_3)_2Ru^{II}(\mu\text{-}Cl_3)Ru^{III}Cl_2(AsPh_3)]$	1962(s) 332, 285(t,w)	600(326);500(sh); 450(1280)
$[(CO)(PPh_3)_2Ru^{II}(\mu\text{-}Cl_3)Ru^{III}Cl_2(AsPh_3)]$	1965(s) 278(t,w),254(b,w)	572(215);424(1450); 376(2291)
$[(CO)(AsPh_3)_2Ru^{II}(\mu\text{-}Cl_3)Ru^{III}Cl_2(PPh_3)]$	1971(s) 301(t,w),231(b,w)	540(164);434(934); 380(1474)
$[(CO)(P\{p\text{-}tol\}_3)_2Ru^{II}(\mu\text{-}Cl_3)Ru^{III}Cl_2(PPh_3)]$	1967(s) 321(t,w)	556(240);404(2032); 360(3401)
$[(CO)(PPh_3)_2Ru^{II}(\mu\text{-}Br_2Cl)Ru^{III}Cl_2(AsPh_3)]$	1968(s) 385,281(t,w), 248(b,w)	578(260);498(868); 408(4783)

*(s) strong; (w) week; (t) terminal; (b) bridge.

**(sh) shoulder; in CH_2Cl_2, solution [*ca.* $10^{-3}-10^{-4}$ M].

intervalence transition to higher energies, as it raises the energy necessary for electron promotion.

The presence of Ru^{III} species in the present binuclear complexes is confirmed by the EPR spectra measured at 9.5 GHz. A typical EPR spectrum characteristic of a magnetically isolated Ru^{III} ion where two g-tensor (g_1 and g_3) values were experimentally observed for our binuclear complexes is shown in Figure 4. By simulation of the powder spectral data, the third g-tensor values (g_2) for the complexes were calculated. The very small difference between g_1 and g_2 imply in a very small rhombic distortion around the Ru^{III} center, compatible with a C_{4v} group around this metal center which was also observed by X-ray structural measurements of [(CO)$(AsPh_3)_2$Ru^{II}(μ-Cl_3) Ru^{III}Cl_2($AsPh_3$)] and [(CO)$(PPh_3)_2$Ru^{II}(μ-Br_3) Ru^{III}Br_2(PPh_3)] complexes (Figs. 2 and 3). It is interesting to point out that the complexes by themselves are of C_s symmetry and that the EPR data show experimentally only two g-tensor values supporting our classification of Class I type for our complexes with an axial symmetry at the Ru^{III} centers.

Our complexes show two reversible redox processes corresponding to the reductions of the Ru^{III} (generation of RuII/RII species) centers in low cathodic regions and the oxidations of the Ru^{II} centers (generation of Ru^{III}/ Ru^{III}) in high anodic regions are observed (Tab. VI, Fig. 5). As expected the electrochemical behavior of the complexes listed at Table VI are very similar

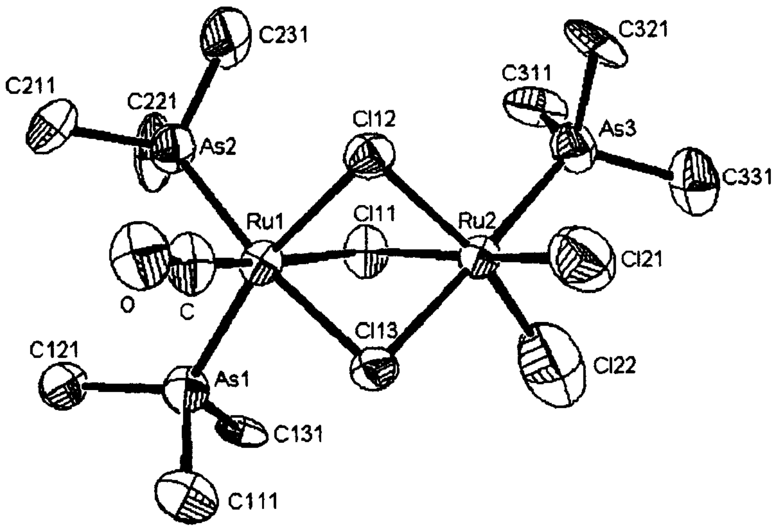

FIGURE 2 Ortep drawing of the [$Ru_2Cl_5(CO)(AsPh_3)_3$].

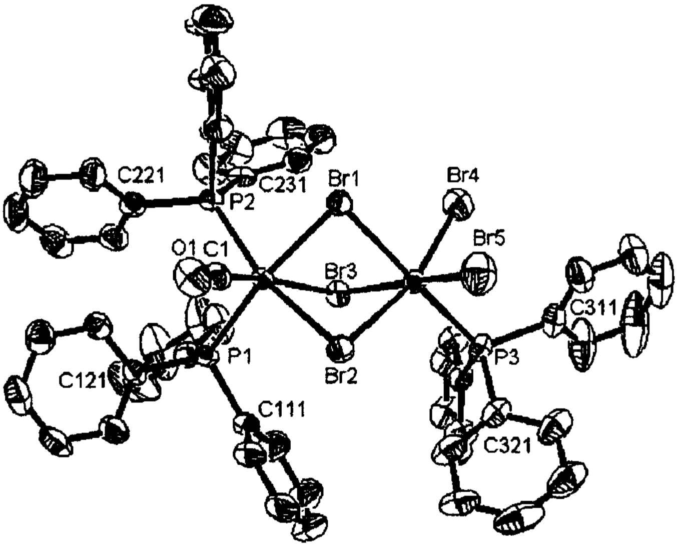

FIGURE 3 Ortep drawing of the $[Ru_2Br_5(CO)(PPh_3)_3]$.

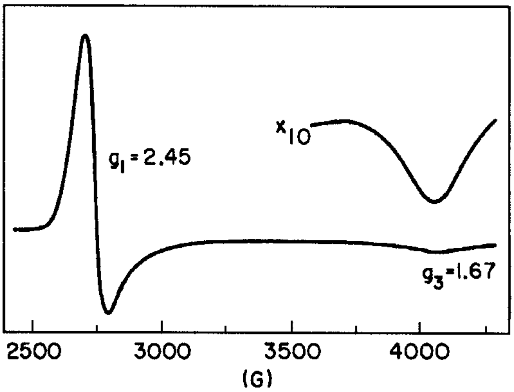

FIGURE 4 EPR spectrum of the $[Ru_2Cl_5(CO)(AsPh_3)_3]$ (X band frequency) at − 160°C in the solid state.

TABLE VI EPR and electrochemical data for binuclear-carbonyl mixed valence complexes

Complexes	g_1	g_2	g_3	$E_{1/2}(1)$	$E_{1/2}(2)$
$[(AsPh_3)Cl_2Ru^{III}\text{-}\mu(Cl_3)\text{-}Ru^{II}(CO)(AsPh_3)_2]$	2.45	–	1.67	−0.25	1.40
$[(PPh_3)Cl_2Ru^{III}\text{-}\mu(Cl_3)\text{-}Ru^{II}(CO)(AsPh_3)_2]$	2.4223	2.4221	1.75	−0.23	1.40
$[(AsPh_3)Cl_2Ru^{III}\text{-}\mu(Cl_3)\text{-}Ru^{II}(CO)(PPh_3)_2]$	2.4580	2.4290	1.75	−0.21	1.44
$[(PPh_3)Cl_2Ru^{III}\text{-}\mu(Cl_3)\text{-}Ru^{II}(CO)(P\{p\text{-}tol\}_3)_2]$	2.4287	2.4277	1.74	−0.24	1.33
$[(AsPh_3)Cl_2Ru^{III}\text{-}\mu(Cl)\mu(Br_2)\text{-}Ru^{II}(CO)(PPh_3)_2]$	2.46	–	1.74	−0.20	1.37

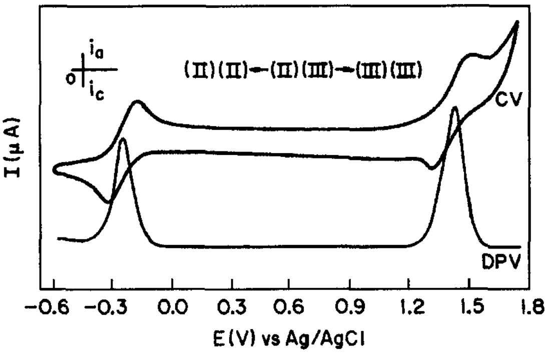

FIGURE 5 Cyclic voltammogram (cv) and differential pulse voltammogram (dpv) of the $[Ru_2Cl_5(CO)(AsPh_3)_3]$; 1.0×10^{-3} M; in CH_2Cl_2 with 0.1 M PTBA; scan rate 100 mV/s (cv) and 20 mV/s (dpv); measured at a Pt electrode. $Fc^+/Fc = 0.43$ V *vs.* Ag/AgCl.

to that shown by the original compound $[Ru_2Cl_5(CO)(PPh_3)_3]$ in the same conditions [7].

SUPPLEMENTARY MATERIAL

The supplementary materials for *ttt*-$[Ru^{II}Cl_2(CO)_2(PPh_3)_2]$, $[(CO)(AsPh_3)_2Ru^{II}(\mu\text{-}Cl_3)Ru^{III}Cl_2(AsPh_3)]$ and $[(CO)(PPh_3)_2Ru^{II}(\mu\text{-}Br_3)Ru^{III}Br_2(PPh_3)]$ were deposited in the CCDC with the numbers 132751, 130267 and 132750, respectively.

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