

# MOLECULAR STRUCTURES, ELECTROCHEMICAL AND SPECTROSCOPICAL PROPERTIES OF DICHLORODICARBONYLBIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II) AND DICHLORODICARBONYLBIS(TRIPHENYLARSINE)RUTHENIUM(II)

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Abstract—The cct isomers  $[RuCl_2(CO)_2(PPh_3)_2]$  (1) and  $[RuCl_2(CO)_2(AsPh_3)_2]$  (2) were synthesized from  $[RuCl_3(PPh_3)_2DMA]DMA$  and  $[RuCl_3(AsPh_3)_2DMA]DMA$ , respectively. The complexes were characterized by elemental analysis, IR and UV-vis spectroscopy and their molecular structures were found to be *cis-cis-trans* isomers by X-ray crystallography. Cyclic voltammetry data show that the triphenylphosphine stabilizes better the ruthenium(II) complex than the triphenylarsine ligand.

In view of the increasing necessity to obtain products of high purity there has been a great deal of interest in catalysts that are capable of performing selective homogeneous processes like the hydrogenation of unsaturated substrates. Transition metal complexes have figured prominently in these reactions as excellent catalysts, in particular, complexes of ruthenium in low oxidation state containing tertiary phosphines in their structures. Thus in 1965 Wilkinson's group have shown that the [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] and [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] are extremely efficient for the reduction of alkenes and alkynes at  $25^{\circ}$ C and 1 atm.<sup>1</sup> The accumulated data on the

use of ruthenium-phosphine systems for hydrogenation reactions is now substantial and it is well known that  $[RuCl_2(CO)_2(PPh_3)_2]$  is a very effective catalyst for the selective hydrogenation of 1,5,9-cyclododecatriene(cyclopolyolefins) to cyclododecene(cyclomonoolefins).<sup>2</sup> In view of the interest in this class of ruthenium compounds we are reporting in this paper a new route for the synthesis of the title complexes, their electrochemical and spectroscopical properties and X-ray structures. Although much information on tertiary phosphine complexes of transition metals is available, relatively little has been reported on complexes containing tertiary arsine. Nevertheless, such compounds are of interest in view of their potential catalytic activities.<sup>3,4</sup> In addition, the ruthenium

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complexes presently being reported are also interesting from the structural point of view, as they lead to a comparison with similar compounds with different ligand distribution around the metal centre.<sup>5,6</sup>

#### **EXPERIMENTAL**

The carbonyl complexes were obtained from  $[\operatorname{RuCl}_3(L)_2 DMA]DMA^7$  (L = PPh<sub>3</sub> or AsPh<sub>3</sub>) (0.2g) in N,N'-dimethylacetamide(DMA), ethanol or dichloromethane (*ca* 5 cm<sup>3</sup>). To the solution was passed a stream of carbon monoxide under reflux. After approximately 3 h the volume of the solution was reduced and deoxygenated ether was added, producing white (PPh<sub>3</sub>) or yellowish (AsPh<sub>3</sub>) solids, which were collected by filtration, washed with hexanes and ether, and dried *in vacuo*. Recrystallization from dichloromethane/ethanol/ether afforded the products as bright crystals. Found: C, 60.4; H, 4.1. Calc. for [RuCl<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] C, 60.6; H, 4.0%. Found: C, 54.2; H, 3.5. Calc. for [RuCl<sub>2</sub>(CO)<sub>2</sub>(AsPh<sub>3</sub>)<sub>2</sub>] C, 54.3; H, 3.6%.

#### X-ray diffraction data

Experimental details on X-ray diffraction are given in Table 1. Data were corrected for Lorentz, polarization and absorption effects, following the procedure of Walker and Stuart.<sup>8</sup> The structure determination and refinement were performed with the SHELX76 system of programs. Fig. 1 was drawn with the ORTEP<sup>9</sup> program.

# Crystal structure determination and refinement

Cell parameters and orientation matrices were obtained from the setting angles of 25 centred reflections in range  $11 < \theta < 21^{\circ}$ the for  $[RuCl_2(CO)_2(PPh_3)_2]$ and  $17 < \theta < 48^{\circ}$ for [RuCl<sub>2</sub>(CO)<sub>2</sub>(ASPh<sub>3</sub>)<sub>2</sub>]. The structures were solved using the standard heavy-atom Patterson method and difference Fourier techniques. In final cycles of blocked-matrix least squares refinement, all non-H atoms were treated anisotropically and H atoms were included as fixed contributors at the positions found in difference Fourier maps with an over-

Compound	1	2 As <sub>2</sub> C <sub>18</sub> Cl <sub>2</sub> H <sub>20</sub> O <sub>2</sub> Ru	
Formula	$C_{38}Cl_2H_{30}O_2P_2Ru$		
Μ	752.59	840.48	
System	Monoclinic	Monoclinic	
Space group	$P2_1/n$	$P2_{1}/n$	
<i>a</i> (Å)	10.364(3)	10.519(1)	
b (Å)	25.913(5)	25.753(1)	
c (Å)	12.634(2)	12.7684(6)	
β (°)	100.29(4)	101.116(7)	
$V(Å^3)$	3338(2)	3393.8(8)	
Z	4	4	
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.497	1.645	
Sample dimensions (mm)	$0.50 \times 0.15 \times 0.10$	$0.30 \times 0.20 \times 0.10$	
$\lambda$ (Å)	(Mo-K <sub>a</sub> ) 0.71073	(Cu-K <sub>n</sub> ) 1.54056	
Linear absorption coefficient ( $\mu$ ) (cm <sup>-1</sup> )	7.48	77.59	
Absorption correction factors	1.07, 0.78	1.26, 0.91	
Scan technique	$\omega/2\theta$	$\omega/2\hat{\theta}$	
$\theta$ range (°)	0-25	0-60	
F (000)	1528	1672	
Reflections measured	5712	5099	
Unique reflections	5405	4873	
<i>R</i> <sub>int</sub>	0.015	0.012	
Reflections above $3\sigma(I)$	4438	4304	
Minimized function	$\Sigma w( F_0  -  F_c )^2$		
Weighting scheme	$[\sigma^2(F_{\rm O}) + 0.00009 F_{\rm O} ^2]^{-1}$	$[\sigma^2(F_{\rm O}) + 0.0001 F_{\rm O} ^2]^{-1}$	
$R = \Sigma[ F_{\rm O}  -  F_{\rm C} ] / \Sigma  F_{\rm O} $	0.033	0.030	
$R_{\rm w} = [\Sigma {\rm w}( F_{\rm O}  -  F_{\rm C} )^2 / \Sigma {\rm w} F_{\rm O} ^2]^{1/2}$	0.034	0.031	
$S = [\Sigma w( F_0  -  F_c )^2 / (M - N)]^{1/2}$	2.14	2.05	
Range $h; k; l$	-12, 12; 0, 30; 0, 15	-11, 11; 0, 28; 0, 14	
Max., min. residual $\rho$ (eÅ <sup>-3</sup> )	0,58, -0.34	0.39, -0.42	

Table 1. Crystal and refinement data for cis-RuCl<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (1) and cis-RuCl<sub>2</sub>(CO)<sub>2</sub>(AsPh<sub>3</sub>)<sub>2</sub> (2)

all isotropic thermal parameter that refined to  $U_{\rm iso} = 0.081(3)$  and  $0.097(4)\text{\AA}^2$  for triphenyl-phosphine and triphenylarsine complexes, respectively.

### Spectroscopic measurements

*IR spectra*. Pellets were prepared from crystalline powder samples diluted in CsI. Measurements were performed on a Bomem-Michelson 102 spectrometer in the region 4000-190 cm<sup>-1</sup>.

*UV-vis spectra*. The electronic spectra were measured in  $CH_2Cl_2$  solutions(10<sup>-4</sup> mol 1<sup>-1</sup>) on a Varian DMS-100 spectrophotometer.

Electrochemistry. The cyclic voltammograms were recorded at  $25.0\pm0.1$  °C in freshly distilled dichloromethane containing 0.1 mol  $1^{-1}$  of tetrabutylammonium perchlorate (TBAP) using an EG & PARC electrochemical system consisting of a model RE 0073 recorder, a model 173 potentiostat and a model 175 universal programmer. A three electrode system consisting of glassy carbon working and a platinum auxiliary electrode was used. The reference electrode was Ag/AgCl (TBAP 0.2 mol  $1^{-1}$  in CH<sub>2</sub>Cl<sub>2</sub>). The working solution was separated from the reference electrode with a Luggin-Haber containing salt bridge, filled with the solvent and supporting electrolyte. Temperature was stabilized with the electrochemical cell immersed in a constant temperature bath. As recommended by IUPAC<sup>10</sup>, the ferrocinium  $(Fc^+)/ferrocene$  (Fc) couple was employed as an internal reference and all potentials reported herein are given in relation to the oxidation potential of the reference electrode (0.55 V). TBAP (Fluka purum) was recrystallized from ethanol/water and dried under vacuum overnight. Dichloromethane was distilled over P<sub>2</sub>O<sub>5</sub> and



Fig. 1. Molecular structure and atom labelling scheme for the isomorphous complexes  $[RuCl_2(CO)_2(L)_2]$  (L = PPh<sub>3</sub> or AsPh<sub>3</sub>).

stored over Linde 4 Å molecular sieves. All working solutions were degassed with prepurified argon before measurements and were kept under an argon blanket during the experiments.

# **RESULTS AND DISCUSSION**

The X-ray structures of the *cis* isomers  $[\operatorname{RuCl}_2(\operatorname{CO})_2(L)_2]$  (L = PPh<sub>3</sub> or AsPh<sub>3</sub>) are shown in Fig. 1. Table 2 lists the relevant bond lengths for these molecules. These data show that the bond lengths involving phosphorus are shorter than those with arsine, as expected, considering the different covalent radii of these atoms. This difference reflects

Table 2. Selected bond distances (Å)

$RuCl_2(CO)_2(PPh_3)_2$ $RuCl_2(CO)_2(AsPh_3)_2$	RuCl <sub>2</sub> (CO) <sub>2</sub> (AsPh <sub>3</sub> ) <sub>2</sub>	
Ru-Cl(1) 2.426(1) $Ru-Cl(1)$ 2.	426(1)	
Ru-Cl(2) 2.453(1) $Ru-Cl(2)$ 2.	443(1)	
Ru-C(1) 1.865(4) $Ru-C(1)$ 1.	873(5)	
Ru-C(2) 1.854(4) $Ru-C(2)$ 1.	848(5)	
Ru - P(1) 2.4247(9) $Ru - As(1)$ 2.	4927(6)	
Ru - P(2) 2.4249(9) $Ru - As(2)$ 2.	4855(6)	
P(1)-C(111) 1.835(4) As(1)-C(111) 1.	955(4)	
P(1) - C(121) 1.837(4) $As(1) - C(121)$ 1.	937(4)	
P(1)-C(131) 1.819(4) $As(1)-C(131)$ 1.	935(5)	
P(2) - C(211) 1.829(4) $As(2) - C(211)$ 1.	.945(4)	
P(2) - C(221) 1.831(4) $As(2) - C(221)$ 1.	.953(4)	
P(2) - C(231) 1.829(4) $As(2) - C(231)$ 1.	.941(5)	
C(1) - O(1) 1.134(5) $C(1) - O(1)$ 1.	112(6)	
C(2) - O(2) 1.127(5) $C(2) - O(2)$ 1.	.142(6)	

also at the longer distances Ru-As [2.4927(6) and 2.4855(6) Å] when compared with Ru-P [2.4247(9) and 2.4249(9) Å]. The Ru-CO distances (ca 1.85 Å) for the title compounds are close to the ones found in the cis-isomer of the complex  $[RuCl_2(CO)_2(BzI_3P)_2]$  (1.863 Å) and shorter than the equivalent bond length for the trans(CO)-isomer of this complex (1.948 Å).<sup>5</sup> This observation can be explained by the stronger trans influence of carbon monoxide when compared with chloride.<sup>6,11,12,13</sup> In the complex  $[RuCl_2(CO)(C_2H_4)(Me_2PPh)_2]$ , where the CO is trans to chlorine, the distance Ru-CO is 1.831 Å<sup>14</sup> and for the [Ru(OAc)(p-MeC<sub>6</sub>H<sub>4</sub>N-CH)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (CO trans to the acetate ion) this distance is 1.81(1) Å.<sup>15</sup> The Ru-Cl bond lengths trans to CO observed in the present work are typically close to 2.4 Å (Table 2), which is fairly similar to those reported in the literature.<sup>5,13,14,16,17</sup> Selected interatomic angles for the -PPh<sub>3</sub> and -AsPh<sub>3</sub> complexes are presented in Table 3. The IR spectrum of the [RuCl<sub>2</sub>(CO)<sub>2</sub>(AsPh<sub>3</sub>)<sub>2</sub>] shows the  $v_{CO}$ at 2059 cm  $^{-1}(s)$  and 1995 cm  $^{-1}(s)$  and  $\nu_{Ru-Cl}$  at 334 and 280 cm<sup>-1</sup>(w). For the  $[RuCl_2(CO)_2(PPh_3)_2]$ complex, these bands are at 2060 and 1998  $cm^{-1}$ 

 $(v_{CO})$  and 302 and 278 cm<sup>-1</sup>  $(v_{Ru-Cl})$ . These values are according to the literature data for *cis* carbonyl isomers where chloride are *trans* to CO.<sup>5,13</sup>

The electronic absorption spectra for these compounds show transitions at high energy: 277 nm,  $\hat{\epsilon}(1.86 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$  and 303 nm,  $\hat{\epsilon}(1.79 \times 10^4 \text{ cm}^{-1})$  $M^{-1}$  cm<sup>-1</sup>) for the phosphine and 281 nm,  $\varepsilon(1.70 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$  and 320 nm,  $\varepsilon(1.27 \times 10^4 \text{ m}^{-1})$  $M^{-1}$  cm<sup>-1</sup>) for the arsine complex, respectively. These bands can be assigned as ligand-to-metal charge transfer (LMCT) transitions. The fact that the triphenylphosphine complex absorbs at higher energy is in accordance to its stronger ligand field when compared with triphenylarsine.<sup>18</sup> These data are further supported by our electrochemical experiments which show higher stability for the  $-PPh_3$  complex (E<sub>1/2</sub> > 2.0 V vs Ag/AgCl) when compared with the  $-AsPh_3$  complex ( $E_{1/2} = 1.1$  V vs Ag/AgCl). Although triphenylphosphine is a better  $\sigma$ -donor ligand than triphenylarsine,<sup>19</sup> our data suggest that for these ruthenium(II) complexes, the triphenylphosphine present stronger  $\pi$ -acceptor character than triphenylarsine ligand. For complexes with general formula  $[RuCl_2(CO)_2(R_3P)_2]$  the

Table 3. Selected interatomic angles (°)

RuCl <sub>2</sub> (CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>		$RuCl_2(CO)_2(AsPh_3)_2$	
Cl(1)— $Ru$ — $Cl(2)$	95.71(3)	Cl(1)— $Ru$ — $Cl(2)$	94.33(4)
Cl(1)— $Ru$ — $C(1)$	177.2(1)	Cl(1)— $Ru$ — $C(1)$	177.9(1)
Cl(1)—Ru—C(2)	93.1(1)	Cl(1)— $Ru$ — $C(2)$	91.9(2)
Cl(1)-Ru-P(1)	87.25(3)	Cl(1)— $Ru$ — $As(1)$	86.97(3)
Cl(1)—Ru—P(2)	88.13(3)	Cl(1)—Ru—As(2)	87.65(3)
Cl(2)— $Ru$ — $C(1)$	81.5(1)	Cl(2)— $Ru$ — $C(1)$	83.7(1)
Cl(2)—RuC(2)	171.1(1)	Cl(2)— $Ru$ — $C(2)$	173.8(2)
Cl(2)RuP(1)	90.30(3)	Cl(2)— $Ru$ — $As(1)$	90.35(3)
Cl(2)RuP(2)	89.27(3)	Cl(2)— $Ru$ — $As(2)$	88.23(3)
C(1)—Ru—C(2)	89.6(2)	C(1)— $Ru$ — $C(2)$	90.1(2)
C(1)— $Ru$ — $P(1)$	93.4(1)	C(1)— $Ru$ — $As(1)$	93.6(1)
C(1) - Ru - P(2)	91.2(1)	C(1)— $Ru$ — $As(2)$	91.7(1)
C(2)— $Ru$ — $P(1)$	89.6(1)	C(2)— $Ru$ — $As(1)$	89.8(1)
C(2)— $Ru$ — $P(2)$	91.5(1)	C(2)— $Ru$ — $As(2)$	92.2(1)
P(1)— $Ru$ — $P(2)$	175.30(3)	As(1)— $Ru$ — $As(2)$	174.32(2)
Ru - P(1) - C(111)	115.6(1)	Ru—As(1)—C(111)	114.6(1)
Ru—P(1)—C(121)	119.3(1)	Ru - As(1) - C(121)	119.6(1)
Ru—P(1)—C(131)	111.1(1)	Ru - As(1) - C(131)	113.6(1)
C(111)P(1)C(121)	102.5(2)	C(111)— $As(1)$ — $C(121)$	102.0(2)
C(111)P(1)C(131)	102.2(2)	C(111) - As(1) - C(131)	100.5(2)
C(121) - P(1) - C(131)	104.2(2)	C(121)— $As(1)$ — $C(131)$	104.0(2)
Ru - P(2) - C(211)	114.9(1)	Ru - As(2) - C(211)	115.5(1)
Ru—P(2)—C(221)	117.4(1)	Ru—As(2)—C(221)	117.8(1)
Ru—P(2)—C(231)	111.1(1)	Ru-As(2)-C(231)	112.1(1)
C(211)—P(2)—C(221)	102.8(2)	C(211)—As(2)—C(221)	102.1(2)
C(211)—P(2)—C(321)	104.2(2)	C(211)— $As(2)$ — $C(231)$	103.0(2)
C(221)—P(2)—C(231)	105.1(2)	C(221)—As(2)—C(231)	104.7(2)

substitution of a methyl for a phenyl group on the phosphine results in an easier oxidation of the metal centre. Therefore the oxidation potentials for the *cct* isomers [RuCl<sub>2</sub>(CO)<sub>2</sub>(Me<sub>3</sub>P)<sub>2</sub>], [RuCl<sub>2</sub>(CO)<sub>2</sub> (PhMe<sub>2</sub>P)<sub>2</sub>] and [RuCl<sub>2</sub>(CO)<sub>2</sub>(Ph<sub>2</sub>MeP)<sub>2</sub>] are 0.97, 1.40 and 1.46 V, respectively, hence lower than for the *cct* [RuCl<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] complex, which did not show any oxidation process in the anodic limit of 2.2 V for the CH<sub>2</sub>Cl<sub>2</sub> solvent. This feature could be understood in terms of an increase of the electron density at the ruthenium centre provided by the more basic phosphine (Me<sub>3</sub>P > PhMe<sub>2</sub>P > Ph<sub>2</sub>MeP > Ph<sub>3</sub>P).<sup>20</sup>

### Supplementary material

Fractional atomic coordinates, isotropic thermal parameters, hydrogen atoms coordinates, complete list of bond distances and angles for both structures reported in this paper have been deposited with the Editor.

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