

Complexes with Functional Phosphines. Part 8.¹ Interconversion Study of $[\text{RuCl}_2\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}\}_2]$, $[\text{RuCl}_2(\text{CO})\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}\}\text{L}]$, and $[\text{RuCl}_2(\text{CO})_2\text{L}_2]$ [$\text{L} = \text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}$] under CO. Synthesis and X-Ray Structure of *mer*- $[\text{RuCl}_3\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}\}\text{L}]^\dagger$

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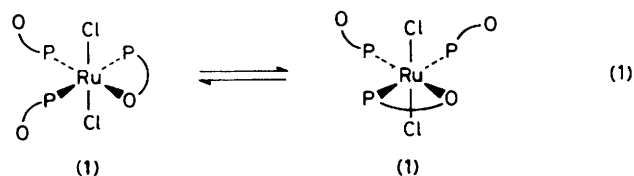
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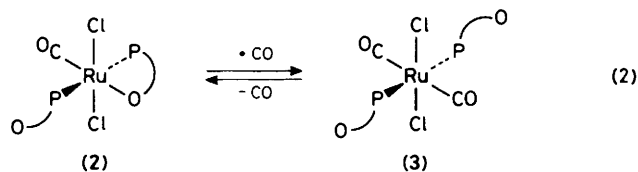
The complex *trans*- $[\text{RuCl}_2\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}\}_2]$ (**1**) [$\text{L} = \text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}$] undergoes a reversible one-electron oxidation at +0.77 V vs. a saturated calomel electrode (s.c.e.) on a Pt electrode in 1,2-dichloroethane containing 0.1 mol dm⁻³ NBu₄ClO₄. A cyclic voltammetric study establishes that under a CO atmosphere, (**1**) is quantitatively converted into *trans,trans,trans*- $[\text{RuCl}_2(\text{CO})_2\text{L}_2]$ (**3**) ($E_3 = +1.65$ V) via *trans*- $[\text{RuCl}_2(\text{CO})\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}\}\text{L}]$ (**2**) ($E_3 = 1.35$ V). Complex (**2**) interconverts with (**3**) via reversible CO co-ordination. Regeneration of (**1**) from (**3**) requires u.v. irradiation in the presence of excess L. The reversible one-electron reduction of *mer,trans*- $[\text{RuCl}_3\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}\}\text{L}]$ (**4**) occurs at -0.22 V. The structure of complex (**4**) was established by a single-crystal X-ray diffraction study. Crystals are orthorhombic, space group *P*2₁2₁2₁ (no. 19), with *Z* = 4 in a unit cell of dimensions *a* = 9.104(2), *b* = 15.511(2), and *c* = 24.190(2) Å. The structure has been refined to *R* 0.034 (*R'* 0.046). The Ru atom has a distorted octahedral environment with the three chlorine atoms in a *mer* relationship. The chelating ligand is characterized by a Ru-P(2) distance of 2.368(2) Å and a relatively short Ru-O(3) distance of 2.143(5) Å. The distance between Ru and the chlorine atom [Cl(1)] *trans* to the co-ordinated ester oxygen is 2.312(2) Å whereas Ru-Cl(2) and Ru-Cl(3) are 2.323(2) and 2.362(2) Å, respectively.

The relevance of unsymmetrical bidentate ligands, especially phosphines, for selectivity effects in homogeneous catalysis is illustrated by several recent examples.²⁻⁴ The co-ordination chemistry of these ligands is therefore of particular interest and is currently being investigated by many research groups.

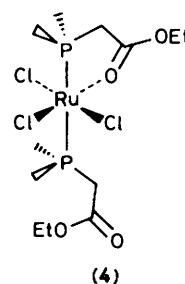
In previous studies where we focused our attention on the co-ordination properties of such ligands,^{1,5,6} we have shown that when ethyl diphenylphosphinoacetate, Ph₂PCH₂C(O)OEt (P(O)), acts as a chelate towards transition metals, easy labilisation of the co-ordinated ester function may occur in solution.^{7,8} Thus, the consequence of the *hemilabile* character of P(O) in complex (**1**) is the dynamic exchange between the *trans* phosphines [equation (1)].⁸ Another property of this



type of ligand is the ability to stabilize 'unsaturated' metal complexes, providing compounds capable of reversible uptake of small molecules such as CO^{8,9} or CO₂.⁵ This point is illustrated by the reaction of complex (**2**) in equation (2).



Because ligand association and substitution processes in chlororuthenium complexes are fundamental steps involved in the reactivity and catalytic properties of such complexes,¹⁰ we have examined in more detail the physicochemical properties of



[†] *mer,trans*-Trichloro(ethyl diphenylphosphinoacetate-*P*)(ethyl diphenylphosphinoacetate-*O,P*)ruthenium(III).

Supplementary data available (No. SUP 56372, 11 pp.): thermal parameters, H-atom co-ordinates, full list of bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii-xx. Structure factors are available from the editorial office.

complexes (1)–(4). Following previous studies on the relationship between the structure and electroactivity of Ru complexes,¹¹ we report here on the electrochemical behaviour of complexes (1)–(4) under argon and under carbon monoxide. The molecular structure of (4) is also described.

Experimental

All solvents were purified and dried by conventional methods and stored under argon. The compounds $\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}$,⁷ $[\text{RuCl}_2\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}\}_2]$ (1),⁸ $[\text{RuCl}_2(\text{CO})_2\text{L}_2]$ (3),⁸ and $[\text{RuCl}_2(\text{CO})\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}\}\text{L}]$ (2)⁸ [L = $\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}$] were prepared as previously described.

Preparation of *mer*- $[\text{RuCl}_3\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}\}\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}\}]$ (4).—A solution of $\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}$ (0.29 g, 1.06 mmol) in ethanol (5 cm³) was slowly added to a mixture of commercial ruthenium trichloride (0.14 g, 0.53 mmol) in ethanol (20 cm³) and aqueous HCl (37%) (2 cm³). After stirring for 15 min, the mixture was filtered. Cooling at –10 °C afforded a dark red powder which was recrystallized from ethanol–hexane, yield 0.45 g (85%), m.p. 166–168 °C (Found: C, 50.75; H, 4.60. Calc. for $\text{C}_{32}\text{H}_{34}\text{Cl}_3\text{O}_4\text{P}_2\text{Ru}$: C, 51.10; H, 4.55%). I.r. (KBr): $\nu(\text{CO})$ (terminal) 1 721s, $\nu(\text{CO})$ (chelating) 1 602s cm⁻¹. U.v., $\lambda_{\text{max.}}(\text{CH}_2\text{Cl}_2)$: 427 and 570 nm.

X-Ray Analysis.—*Crystal data.* $\text{C}_{32}\text{H}_{34}\text{Cl}_3\text{O}_4\text{P}_2\text{Ru}$, $M = 752.0$, orthorhombic, $a = 9.104(2)$, $b = 15.511(2)$, $c = 24.190(2)$ Å, $U = 3 416$ Å³ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710 73$ Å), space group $P2_12_12_1$ (no. 19), $Z = 4$, $D_c = 1.46$ g cm⁻³, $F(000) = 1 532$. Dark red crystals of dimensions $0.20 \times 0.10 \times 0.10$ mm, $\mu(\text{Mo-K}\alpha) = 8.11$ cm⁻¹.

Data collection and processing. Nonius CAD4 diffractometer, $\omega/2\theta$ mode with ω scan width = $1 + 0.35 \tan \theta$, counter aperture $D = (2.00 + 0.50 \tan \theta)$ mm, graphite-monochromated Mo-K α radiation; 4 615 reflections measured ($1 < \theta < 28^\circ$), giving 2 540 independent reflections with $I > \sigma(I)$.

Structure analysis and refinement. The crystal structure was solved using the MULTAN program¹² and refined by full-

matrix least squares with anisotropic thermal parameters for all the non-hydrogen atoms. Hydrogen atoms were introduced by their computed co-ordinates in structure factor calculations but not refined. The final difference map showed no significant maximum. The weighting scheme, $w = [4\sigma(I)^2/I + (0.07 I)^2]^{-1}$, from counting statistics gave satisfactory agreement analyses. Final R and R' values were 0.034 and 0.046 respectively. Computations were carried out on an PDP11/60 computer using the Enraf-Nonius SDP program system.¹³

The final fractional atomic co-ordinates are listed in Table 1.

Electrochemistry.—The experimental results were obtained on a platinum rotating disc electrode (area 3.14 mm², 2 000 revolutions min⁻¹) in 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ containing 0.1 mol dm⁻³ tetrabutylammonium perchlorate under an argon or CO atmosphere (1 atm) [electroactivity range: +1.8 to –1.8 V vs. saturated calomel electrode (s.c.e.)]. The three-electrode cell involved a Pt working electrode, a Pt wire auxiliary electrode, and s.c.e. as reference, the last being in electrical contact with the cell through a junction bridge filled with the same organic solvent and supporting electrolyte as the studied solution. The apparatus used was a Bruker E 130M potentiostat associated with a high-impedance millivoltmeter. The complexes were studied by rotating disc electrode voltammetry, cyclic voltammetry, and controlled potential coulometry.

Results and Discussion

Molecular Structure of Complex (4).—The molecular structure of (4) is shown in Figure 1. Relevant interatomic distances and bond angles are reported in Table 2. Selected least-squares planes are given in Table 3.

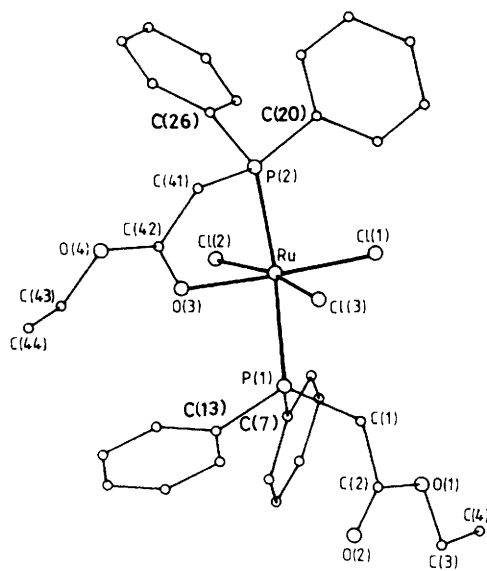
The X-ray study revealed a distorted octahedral arrangement with the three chlorines in a *mer* relationship, the two phosphorus atoms in *trans* positions with respect to each other, and the oxygen (C=O) of one of the esters occupying the sixth co-ordination site. This distortion may be ascribed in part to the occurrence of chelating behaviour for one of the co-ordinated phosphines. Thus the bite angle of the phosphine chelate $[\text{P}(2)\text{-Ru-O}(3) 80.6(2)^\circ]$ is analogous to those found in the Ru^{II} complexes $[\text{RuCl}_2\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}\}\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}\}]$

Table 1. Fractional atomic co-ordinates with estimated standard deviations in parentheses for *mer*- $[\text{RuCl}_3\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}\}\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{OEt}\}]$ (4)

Atom	x	y	z	Atom	x	y	z
Ru	0.107 01(5)	–0.003 92(3)	0.663 51(2)	C(14)	0.267 0(9)	–0.162 5(5)	0.549 0(4)
Cl(1)	–0.004 5(2)	0.129 1(1)	0.654 05(9)	C(15)	0.355(1)	–0.235 4(5)	0.543 5(4)
Cl(2)	–0.090 6(2)	–0.081 0(1)	0.628 12(9)	C(16)	0.502(1)	–0.229 5(6)	0.550 5(4)
Cl(3)	0.330 7(2)	0.053 8(1)	0.696 41(8)	C(17)	0.565(1)	–0.151 6(7)	0.562 6(4)
P(1)	0.206 3(2)	0.007 1(1)	0.572 91(7)	C(18)	0.481 5(9)	–0.078 2(6)	0.568 3(4)
P(2)	0.034 9(2)	–0.028 1(1)	0.756 29(8)	C(20)	0.043 6(8)	0.054 6(5)	0.810 6(3)
O(1)	0.269 8(7)	0.186 9(4)	0.485 4(3)	C(21)	–0.003 9(9)	0.035 7(5)	0.863 5(3)
O(2)	0.460 4(7)	0.096 5(4)	0.483 7(3)	C(22)	0.006(1)	0.098 8(6)	0.904 0(4)
O(3)	0.206 3(5)	–0.127 5(3)	0.676 5(2)	C(23)	0.061(1)	0.180 1(5)	0.891 0(4)
O(4)	0.267 3(6)	–0.233 0(3)	0.734 5(2)	C(24)	0.109(1)	0.197 8(5)	0.839 3(4)
C(1)	0.313 6(9)	0.106 9(5)	0.564 9(3)	C(25)	0.099(1)	0.135 5(5)	0.797 5(3)
C(2)	0.362 0(9)	0.128 6(4)	0.508 1(3)	C(26)	–0.134 2(7)	–0.086 0(4)	0.769 6(3)
C(3)	0.296(1)	0.212 4(6)	0.429 0(4)	C(27)	–0.261 8(9)	–0.050 8(6)	0.747 9(4)
C(4)	0.173(1)	0.262 5(8)	0.410 2(5)	C(28)	–0.394(1)	–0.089 8(7)	0.757 7(4)
C(7)	0.086 9(8)	0.010 5(4)	0.510 8(3)	C(29)	–0.403(1)	–0.165 5(6)	0.788 4(4)
C(8)	0.139 3(8)	–0.014 5(5)	0.459 5(3)	C(30)	–0.277 2(9)	–0.201 8(5)	0.808 5(4)
C(9)	0.051(1)	–0.005 6(6)	0.412 7(3)	C(31)	–0.142 9(8)	–0.161 9(5)	0.799 5(4)
C(10)	–0.086(1)	0.027 3(7)	0.418 5(4)	C(41)	0.183 4(8)	–0.103 3(5)	0.774 2(3)
C(11)	–0.141(1)	0.052 7(7)	0.468 9(4)	C(42)	0.219 4(7)	–0.156 4(4)	0.724 3(3)
C(12)	–0.054 5(9)	0.043 2(5)	0.515 9(3)	C(43)	0.310(1)	–0.287 5(6)	0.687 7(4)
C(13)	0.330 1(8)	–0.083 5(5)	0.560 2(3)	C(44)	0.433(2)	–0.330 9(9)	0.697 9(6)

Table 2. Selected interatomic distances (Å) and angles (°) for *mer*-[RuCl₃{Ph₂PCH₂C(O)OEt}{Ph₂PCH₂C(O)OEt}] (4)

Ru-Cl(1)	2.312(2)	O(1)-C(3)	1.440(12)
Ru-Cl(2)	2.323(2)	O(2)-C(2)	1.183(10)
Ru-Cl(3)	2.362(2)	O(3)-C(42)	1.245(9)
Ru-P(1)	2.377(2)	O(4)-C(42)	1.289(8)
Ru-P(2)	2.368(2)	O(4)-C(43)	1.466(11)
Ru-O(3)	2.143(5)	C(3)-C(4)	1.44(2)
P(1)-C(1)	1.840(9)	C(41)-C(42)	1.498(11)
P(2)-C(41)	1.839(7)	C(43)-C(44)	1.33(2)
O(1)-C(2)	1.350(10)	Mean C-C-C in phenyl ring	1.381(12)
Cl(1)-Ru-Cl(2)	94.74(7)	Ru-P(1)-C(1)	111.0(3)
Cl(1)-Ru-Cl(3)	94.24(7)	Ru-P(2)-C(41)	96.9(3)
Cl(1)-Ru-P(1)	90.68(8)	C(2)-O(1)-C(3)	117.8(8)
Cl(1)-Ru-P(2)	96.49(7)	Ru-O(3)-C(42)	119.9(5)
Cl(1)-Ru-O(3)	177.1(2)	C(42)-O(4)-C(43)	118.2(7)
Cl(2)-Ru-Cl(3)	170.56(8)	P(1)-C(1)-C(2)	116.5(6)
Cl(2)-Ru-P(1)	89.52(8)	O(1)-C(2)-O(2)	123.3(8)
Cl(2)-Ru-P(2)	93.05(8)	O(1)-C(2)-C(1)	110.2(7)
Cl(2)-Ru-O(3)	85.4(2)	O(2)-C(2)-C(1)	126.3(9)
Cl(3)-Ru-P(1)	87.46(7)	O(1)-C(3)-C(4)	109.0(1)
Cl(3)-Ru-P(2)	88.83(7)	P(2)-C(41)-C(42)	108.6(6)
Cl(3)-Ru-O(3)	85.8(2)	O(3)-C(42)-O(4)	122.8(7)
P(1)-Ru-P(2)	172.15(7)	O(3)-C(42)-C(41)	122.0(6)
P(1)-Ru-O(3)	92.2(2)	O(4)-C(42)-C(41)	115.1(7)
P(2)-Ru-O(3)	80.6(2)	O(4)-C(43)-C(44)	112.0(1)

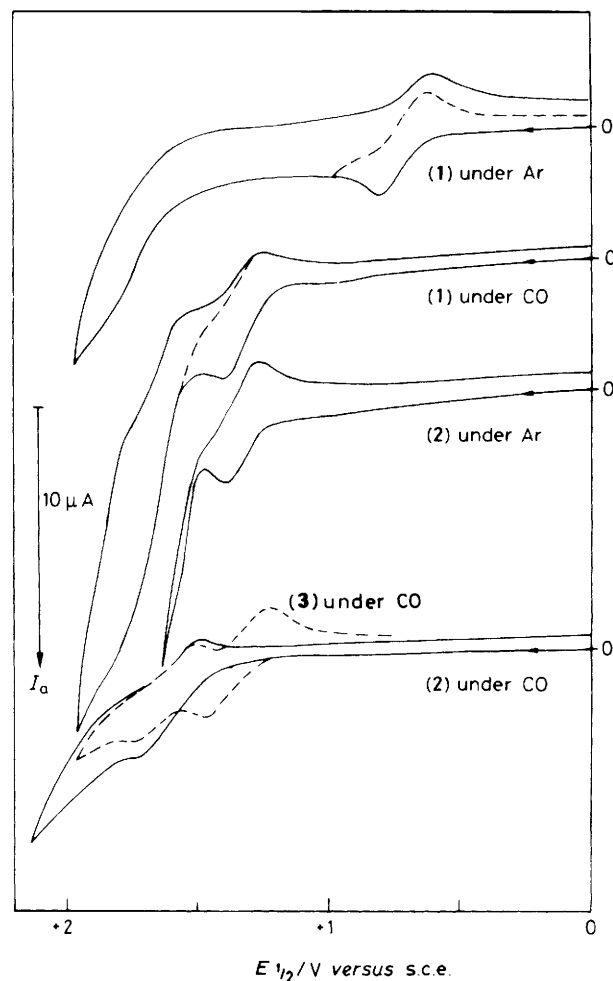
**Figure 1.** Perspective drawing of [RuCl₃{Ph₂PCH₂C(O)OEt}{Ph₂PCH₂C(O)OEt}] (4)

OEt₂] (1) [79.3(1)°]⁸ and [RuCl₂{Ph₂P(*o*-C₆H₄OMe)₂}] [78.81(7) and 79.47(7)°].⁹ The *trans* chlorines are each bent away from Cl(1) and towards the co-ordinated oxygen by *ca.* 5°. This resembles the situation found in (1) where a monodentate Ph₂PCH₂C(O)OEt replaces Cl(1) of (4). Although intramolecular non-bonding interactions should not be neglected, this bending seems to be related to the presence of a weak ligand [O(3)] in the sixth co-ordination position about ruthenium, inducing the observed slight distortion towards a trigonal bipyramid. There is no other published Ru^{III}-O bond distance comparable to that in (4). As expected, the Ru-O(3) bond

Table 3. Least-squares planes for *mer*-[RuCl₃{Ph₂PCH₂C(O)OEt}{Ph₂PCH₂C(O)OEt}] (4); * equations of the planes take the form $Ax + By + Cz + D = 0$

Plane	Atoms	Distance from plane/Å			
		Ru	P(2)	C(41)	C(42)
Plane 1	Ru	-0.002(1)			
	P(2)	0.033(2)			
	C(41)	-0.554(7)			
	C(42)	-0.010(7)			
Plane 2	O(3)	0.200(5)			
	Ru	-0.006(1)			
	Cl(1)	-0.008(2)			
	Cl(2)	0.058(2)			
	Cl(3)	0.050(2)			
O(3)	-0.112(5)				
Plane	A	B	C	D	
1	-0.7923	-0.5288	-0.3045	-5.6249	
2	0.3592	0.0724	-0.9304	-14.5831	

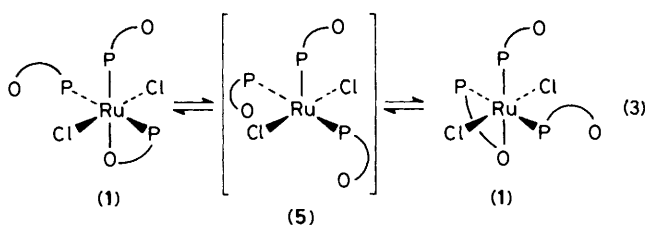
* Dihedral angle between planes 1 and 2 = 92.3°.

**Figure 2.** Cyclic voltammetry of (1)–(3) (*ca.* 5×10^{-4} mol dm⁻³) in 1,2-C₂H₄Cl₂ (0.1 mol dm⁻³ NBu₄ClO₄) under argon or CO. Scan rate = 0.1 V s⁻¹; Pt electrode

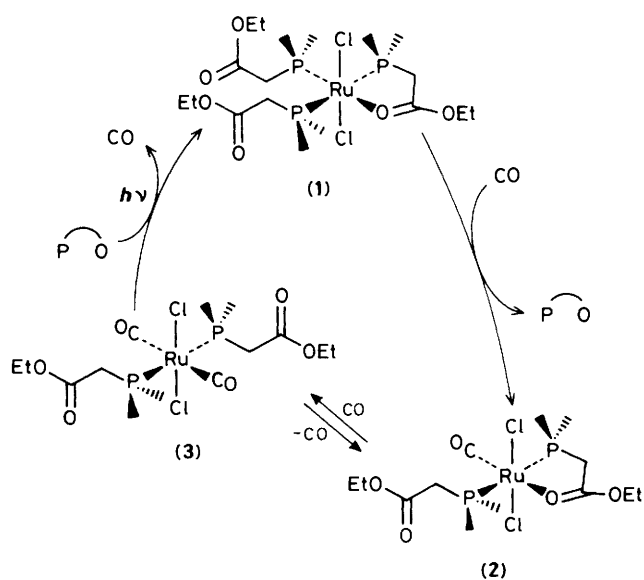
length [2.143(5) Å] is shorter than the corresponding Ru–O bond in the dynamic Ru^{II} complex (1) [2.230(3) Å].⁸ However, this does not allow any conclusion to be drawn about the occurrence of ester exchange on the Ru^{III} centre in solution since n.m.r. studies were precluded by the paramagnetism of the complex. Interestingly, we note that the observed Ru–O distance [2.143(5) Å] is one of the shortest reported in the literature^{8,9,14} and is only slightly longer than the sum of the covalent radii (1.99 Å).¹⁵

The shortest ruthenium–chlorine bond is Ru–Cl(1), involving the chlorine atom *trans* to the oxygen atom of weaker *trans* influence. Other bond lengths and angles in this molecule appear to be normal.

Electrochemistry.—Complex (1) undergoes a reversible one-electron oxidation at $E_{\frac{1}{2}} = +0.77$ V *vs.* s.c.e. under an argon atmosphere (see Figure 2). This value is very close to that measured under the same conditions for the related complex [RuCl₂(PPh₃)₃] ($E_{\frac{1}{2}} = +0.80$ V), indicating that the overall electronic effects of the three phosphines are very similar in each case. This observation and the similar σ -donor– π -acceptor properties of PPh₃ and Ph₂PCH₂C(O)OEt, when acting as P-monodentate ligands,⁷ suggests as a possible intermediate in the dynamic process shown in equation (3) a five-co-ordinated 16-



electron complex. This five-co-ordinate d^6 complex (5) is likely to have a (distorted) square-pyramidal geometry, as favoured theoretically¹⁶ and by analogy with the structures of [RuCl₂(PPh₃)₃]¹⁷ and [Ru(C≡CPh)(PMe₂Ph)₄]PF₆.¹⁸ Note, however, that five-co-ordinate Ru^{II} complexes of the type [Ru(diphosphine)₂Cl]⁺ have been recently reported to have a trigonal-bipyramidal structure, based on their ³¹P n.m.r. spectra.¹⁹



Scheme.

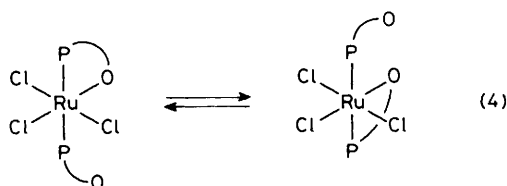
When CO is bubbled through a solution of (1), its oxidation peak disappears within a few seconds and a new peak appears near +1.35 V. On prolonged bubbling the latter peak diminishes in intensity and a new peak appears near +1.65 V. In order to identify the species obtained at +1.35 and +1.65 V we have studied separately the electrochemical oxidations of (2) and (3). Thus complex (2) undergoes a reversible one-electron oxidation step at $E_{\frac{1}{2}} = +1.35$ *vs.* s.c.e. under argon. When CO is bubbled through the solution its wave disappears within a few minutes and a new wave appears at $E_{\frac{1}{2}} = +1.65$ V *vs.* s.c.e. A separate experiment showed the one-electron oxidation of (3) under a CO atmosphere to occur reversibly at +1.65 V *vs.* s.c.e. (Figure 2). These observations clearly establish the rapid step-wise conversions of (1) into (2) and (2) into (3) which occur by reacting the corresponding complexes with CO⁸ (Scheme).

The inability of Ru^{II} to accommodate the necessary back-bonding of three CO ligands and a phosphine accounts for the fact that no further substitution occurs in (3).

The reverse conversion of complex (3) into (2) (by continuous argon bubbling) is complete only after *ca.* 10 h. After this is achieved formation of complex (1) is not observed, even upon addition of an excess of the free ligand Ph₂PCH₂C(O)OEt.

The $E_{\frac{1}{2}}^{\text{ox}}$ obtained for (1), (2), and (3) are in agreement with a decreasing electronic density on the Ru^{II} centre since the phosphine ligands are successively replaced by CO ligands of stronger π -acceptor– σ -donor properties. Thus the $E_{\frac{1}{2}}^{\text{ox}}$ of the Ru^{II}–Ru^{III} couples strongly depends on the donor effects of the co-ordinated ligands. Comparison of the oxidation potentials of (1), (2), and (3) shows that the replacement of a monodentate P(O) ligand by a CO ligand [(1) → (2)] results in an anodic shift of 580 mV, whereas replacement of the co-ordinated –C(O)OEt by CO [(2) → (3)] results in an anodic shift of only 300 mV. This illustrates the strong dissymmetric electronic properties of Ph₂PCH₂C(O)OEt. Although this ligand is irreversibly oxidized near 1.5 V *vs.* s.c.e. (with electrode passivation), its oxidation peak cannot be distinguished on the cyclic voltammogram curves of complexes (1)–(4), even under CO.

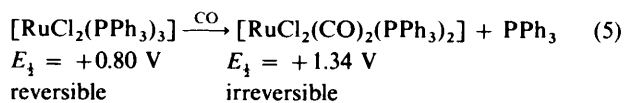
Reduction of the Ru^{III} complex (4) (even under CO) occurs at $E_{\frac{1}{2}} = -0.22$ V *vs.* s.c.e., in the range found for other *mer*-[RuCl₃L₂L'] complexes (*e.g.*: L = organonitrile, L' = MeOH;¹¹ L = arsine, L' = pyridine²⁰). This reversible one-electron reduction is not affected by the presence of CO, confirming the rigidity of the P(O) chelate in (4). Therefore, an exchange process between the functional phosphines of (4) as shown in equation (4), appears unlikely. Because of the



paramagnetism of (4) this phenomenon could not be examined by n.m.r. spectroscopy.

In conclusion, we have shown that the rapid carbonylation of (1) to (3) occurs in two steps *via* the isolable complex (2). Electrochemical experiments have confirmed that under normal conditions (3) can be slowly converted back to (2) by bubbling argon through the solution, but not back to (1). The quantitative conversion of (3) to (1) requires photochemical activation (u.v. lamp) in the presence of free Ph₂PCH₂C(O)OEt in excess.

The sequence of reactions shown in the Scheme contrasts with the one-step *irreversible* reaction (5) observed when CO is bubbled into a solution of [RuCl₂(PPh₃)₃].¹⁰



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References

- 1 Part 7, P. Braunstein, J. Fischer, D. Matt, and M. Pfeffer, *J. Am. Chem. Soc.*, 1984, **106**, 440.
- 2 M. Peuckert and W. Keim, *Organometallics*, 1983, **2**, 594.
- 3 M. Bressan, F. Morandini, and P. Rigo, *J. Organomet. Chem.*, 1983, **247**, C8.
- 4 W. S. Knowles, M. J. Sebacky, and B. D. Vineyard, *Adv. Chem. Ser.*, 1974, **132**, 274.
- 5 P. Braunstein, D. Matt, Y. Dusausoy, J. Fischer, A. Mitschler, and L. Ricard, *J. Am. Chem. Soc.*, 1981, **103**, 5115.
- 6 P. Braunstein, D. Matt, Y. Dusausoy, and J. Fischer, *Organometallics*, 1983, **2**, 1410.
- 7 P. Braunstein, D. Matt, F. Mathey, and D. Thavard, *J. Chem. Res.*, 1978, (S) 232, (M) 3041.
- 8 P. Braunstein, D. Matt, and Y. Dusausoy, *Inorg. Chem.*, 1983, **22**, 2043.
- 9 J. C. Jeffrey and T. B. Rauchfuss, *Inorg. Chem.*, 1979, **18**, 2658.
- 10 F. H. Jardine, *Prog. Inorg. Chem.*, 1984, **31**, 265.
- 11 A. Giraudeau, P. Lemoine, M. Gross, J. Rosé, and P. Braunstein, *Inorg. Chim. Acta*, 1982, **62**, 117.
- 12 G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, 1971, **27**, 368.
- 13 B. A. Frenz, 'Enraf-Nonius CAD4-SDP Computing in Crystallography,' eds. H. Schenk, Orthof-Hazekamp, H. Van Koningsveld, and G. S. Bassi, University Press, Delft, Holland, 1979, p. 64.
- 14 M. M. De V. Steyn, R. B. English, T. V. Ashworth, and E. Singleton, *J. Chem. Res.*, 1981, (S) 267, (M) 3149.
- 15 L. Pauling, 'Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.
- 16 R. G. Pearson, *J. Am. Chem. Soc.*, 1969, **91**, 4947.
- 17 S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 778.
- 18 T. V. Ashworth, A. A. Chalmers, and E. Singleton, *Inorg. Chem.*, 1985, **24**, 2125.
- 19 J. C. Briggs, C. A. McAuliffe, and G. Dyer, *J. Chem. Soc., Dalton Trans.*, 1984, 423.
- 20 R. Contreras, G. A. Heath, A. J. Lindsay, and T. A. Stephenson, *J. Organomet. Chem.*, 1979, **179**, C55.

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