

CYCLOMETALLATION REACTIONS

XIX *. CRYSTAL AND MOLECULAR STRUCTURES OF A CYCLOMETALLATED COMPLEX OF RUTHENIUM, $\text{Ru}\{\text{P}(\text{OC}_6\text{H}_3\text{Me})(\text{OC}_6\text{H}_4\text{Me-4})_2\}_2(\text{CO})_2$

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Summary

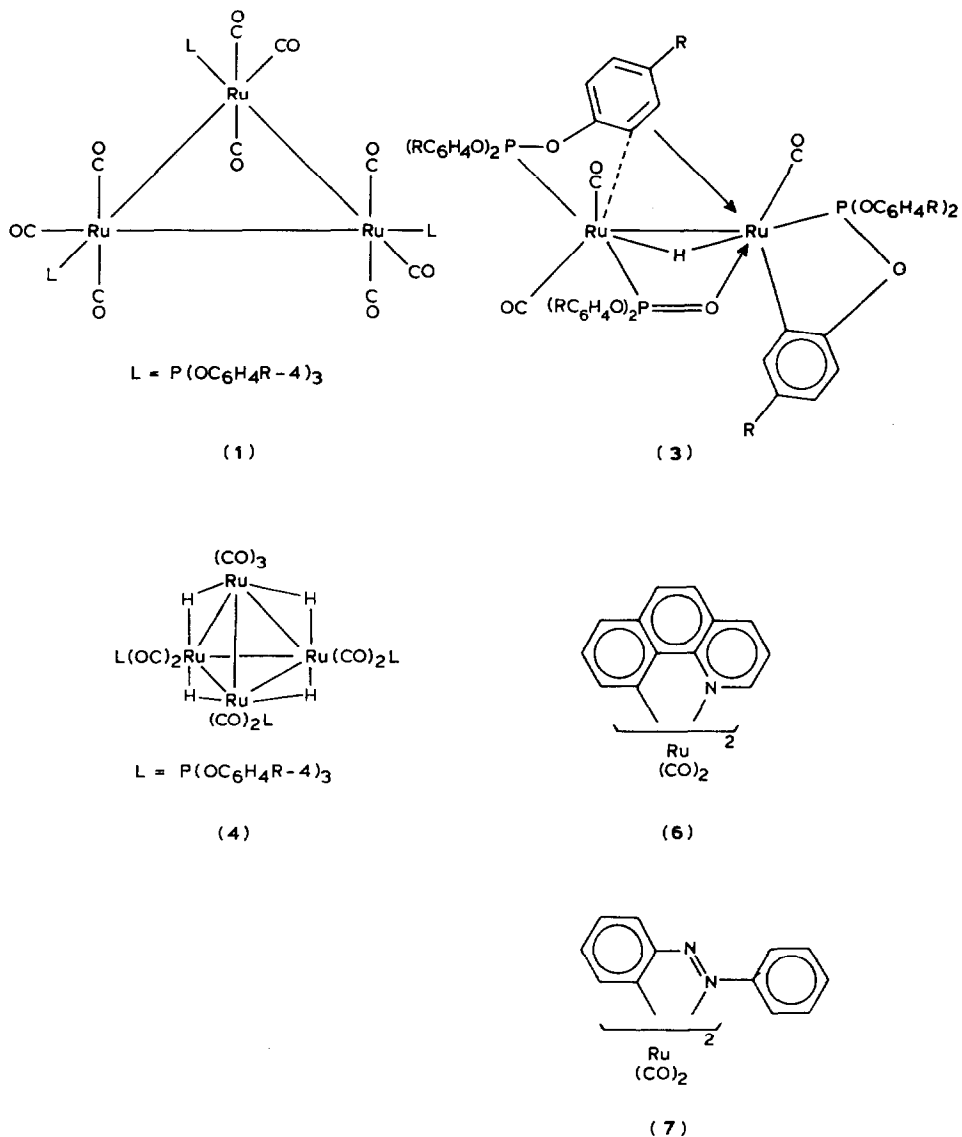
The crystal structure of $\text{Ru}\{\text{P}(\text{OC}_6\text{H}_3\text{Me})(\text{OC}_6\text{H}_4\text{Me-4})_2\}_2(\text{CO})_2$ is reported. The ruthenium atom geometry is distorted octahedrally with two *ortho*-metallated phosphite ligands (with *cis*-P atoms) and two *cis* carbonyls. Crystals are monoclinic, space group $P2_1/c$ with unit cell parameters a 18.552(3), b 12.160(2), c 18.707(4) Å, β 103.38(1)° with $Z = 4$. The structure was refined by a full-matrix least-squares procedure on 4033 unique reflections with $I \geq 2.5\sigma(I)$ to a final R of 0.051.

Introduction

Several years ago, the controlled pyrolysis of the trinuclear cluster complexes $\text{Ru}_3(\text{CO})_9\{\text{P}(\text{OC}_6\text{H}_4\text{R})_3\}_3$ ($\text{R} = \text{H}$ or Me) was reported to give mono-, bi- and tetranuclear complexes $\text{Ru}(\text{CO})_2\{\text{P}(\text{OC}_6\text{H}_3\text{R})(\text{OC}_6\text{H}_4\text{R})_2\}_2$ (**2a**, $\text{R} = \text{H}$; **2b**, $\text{R} = \text{Me}$; Fig. 1) $\text{Ru}_2(\mu\text{-H})\{\mu\text{-OP}(\text{OC}_6\text{H}_4\text{R})_2\}(\text{CO})_3\{\text{P}(\text{OC}_6\text{H}_3\text{R})(\text{OC}_6\text{H}_4\text{R})_2\}_2$ (**3**) and $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_9\{\text{P}(\text{OC}_6\text{H}_4\text{R})_3\}_3$ (**4**) [1]. The molecular structure of complexes **1**, **3** and **4** are now known with reasonable certainty, based on the X-ray structures of $\text{Ru}_3(\text{CO})_9(\text{PMe}_2)_3$ [2], of **3** ($\text{R} = \text{H}$) [3], and of $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_9(\text{PMe}_2\text{Ph})\{\text{P}(\text{OC}_6\text{H}_4\text{Me-4})_3\}\{\text{P}(\text{OCH}_2)_3\text{CEt}\}$ [4]. However, until now it has not been possible to assign any of the four possible structures (excluding optical isomers) (see Fig. 1) to **2**; the IR $\nu(\text{CO})$ spectrum indicates that the two CO groups must occupy mutually *cis* coordination positions. Recently, the molecular structure of $\text{Ru}\{\text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2\}_2\{\text{P}(\text{OPh})_3\}_2$ has been determined as **5** [5]; this corresponds to isomer *c*, with the all *cis* arrangements of the two aryl groups, two metallated

* For part XVIII see ref. 6.

phosphite P atoms, and two $P(OPh)_3$ ligands. We have recently determined the structures of two examples of $Ru(CO)_2$ complexes containing metallated *N*-donor ligands, namely, $Ru(bq)_2(CO)_2$ (**6**; *bq* = benzo[*h*]quinolin-10-yl- C^{10},N) [6] and $Ru(C_6H_4N_2Ph)_2(CO)_2$ (**7**) [7]. These two complexes have differing arrangements of the metallated aryl carbon and associated donor atom, corresponding to **b** and **c**, respectively. This Paper describes the molecular structure of **2b** and makes a comparison with that of **5**.



Experimental

The complex was obtained as described earlier [1] and X-ray quality crystals were obtained from a diethyl ether/methanol mixture.

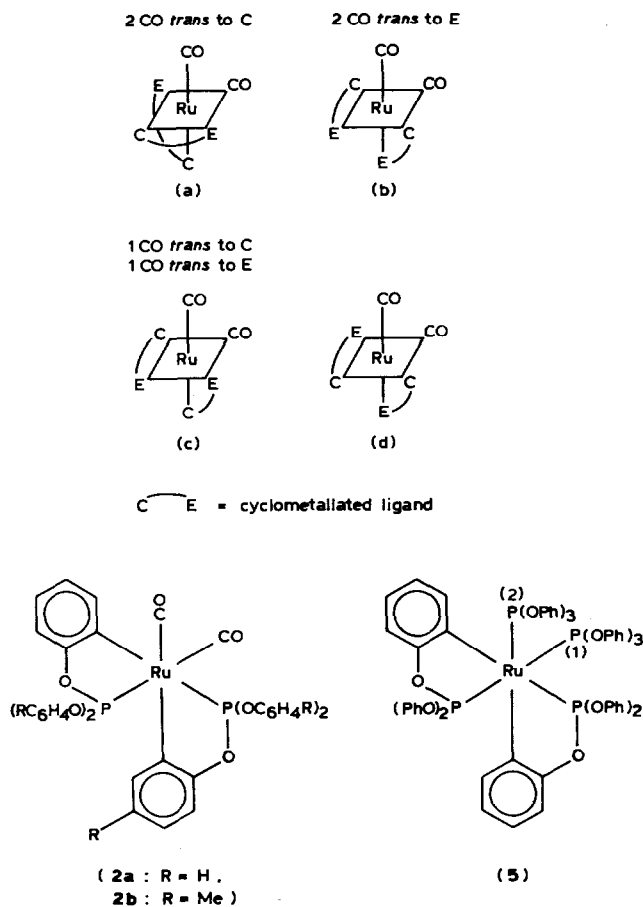


Fig. 1. Possible geometries of octahedral *cis*-Ru(CO)₂(E-C)₂ complexes, and determined structures of complexes 2b and 5.

Crystallography

Intensity data were measured at room-temperature on an Enraf-Nonius CAD4-F diffractometer with the use of Mo- K_{α} (graphite monochromator) radiation, $\lambda = 0.71073 \text{ \AA}$, and the ω - 2θ scan technique. No significant decomposition of the crystal occurred during the data collection. Corrections were applied for Lorentz and polarization effects [8] and for absorption; max. and min. transmission factors were 0.9222 and 0.8818 [8]. Of the 5865 reflections measured in the range $1.2 \leq \theta \leq 22.5^{\circ}$, 5351 were unique and of these, 4033 satisfied the $I \geq 2.5\sigma(I)$ criterion of observability.

Crystal data. $\text{C}_{44}\text{H}_{40}\text{O}_8\text{P}_2\text{Ru}$, $M = 859.8$, monoclinic, space group $P2_1/c$ (C_{2h}^5 , No. 14), a 18.552(3), b 12.160(2), c 18.707(4) \AA , β 103.38(1) $^{\circ}$, U 4105.6 \AA^3 , $Z = 4$, D_x 1.391 g cm^{-3} , $F(000) = 1768$ electrons, $\mu(\text{Mo-}K_{\alpha})$ 4.66 cm^{-1} .

The interpretation of the Patterson synthesis enabled the location of the Ru atom and remaining atoms were located from subsequent difference maps. The structure was refined by a full-matrix least-squares procedure based on F [8]. Anisotropic

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TABLE 1. FRACTIONAL ATOMIC COORDINATES FOR Ru(P(OC₆H₃Me)(OC₆H₄Me-4)₂)(CO)₂ (2b) ($\times 10^5$ for Ru, $\times 10^4$ for other atoms)

Atom	x	y	z
Ru	17872(3)	6572(4)	15217(3)
P(1)	2934(1)	-88(2)	1661(1)
P(2)	2210(1)	2400(1)	1532(1)
C(1)	1725(4)	639(6)	2541(4)
O(1)	1648(4)	684(5)	3117(3)
C(2)	743(4)	931(6)	1123(4)
O(2)	141(3)	1009(5)	831(3)
O(3)	2833(2)	-1372(3)	1475(2)
O(4)	3435(3)	338(4)	1135(3)
O(5)	3569(2)	-70(4)	2414(2)
O(6)	2337(3)	2678(4)	734(3)
O(7)	2997(2)	2639(4)	2070(3)
O(8)	1770(2)	3465(3)	1716(3)
C(3)	2114(4)	-1806(5)	1449(3)
C(4)	1534(4)	-1074(6)	1435(3)
C(5)	836(4)	-1558(6)	1425(4)
C(6)	768(4)	-2704(6)	1463(4)
C(7)	13(5)	-3206(7)	1495(5)
C(8)	1379(5)	-3389(6)	1489(4)
C(9)	2061(4)	-2922(6)	1478(4)
C(14)	5297(7)	-2230(9)	-254(7)
C(21)	3264(6)	-1255(11)	5278(5)
C(24)	2115(4)	1837(6)	205(3)
C(25)	1855(3)	839(5)	398(3)
C(26)	1642(4)	62(6)	-165(4)
C(27)	1700(4)	270(7)	-897(4)
C(28)	1480(5)	-592(8)	-1498(4)
C(29)	1973(4)	1327(7)	-1061(4)
C(30)	2179(4)	2101(7)	-511(4)
C(35)	4746(5)	6532(7)	2291(6)
C(42)	-1359(4)	3676(9)	656(5)
C(11)	4514(3)	-827(4)	1232(2)
C(12)	4972(3)	-1436(4)	885(2)
C(13)	4801(3)	-1527(4)	121(2)
C(15)	4172(3)	-1010(4)	-297(2)
C(16)	3714(3)	-400(4)	50(2)
C(10)	3885(3)	-309(4)	814(2)
C(18)	3231(3)	-1419(3)	3229(2)
C(19)	3164(3)	-1708(3)	3932(2)
C(20)	3310(3)	-932(3)	4497(2)
C(22)	3521(3)	133(3)	4358(2)
C(23)	3588(3)	422(3)	3654(2)
C(17)	3442(3)	-354(3)	3090(2)
C(32)	3252(2)	4492(4)	2525(3)
C(33)	3684(2)	5442(4)	2585(3)
C(34)	4256(2)	5512(4)	2218(3)
C(36)	4397(2)	4632(4)	1791(3)
C(37)	3965(2)	3683(4)	1731(3)
C(31)	3393(2)	3613(4)	2099(3)
C(39)	704(2)	3688(4)	703(2)
C(40)	-63(2)	3758(4)	452(2)
C(41)	-519(2)	3658(4)	946(2)
C(43)	-208(2)	3488(4)	1691(2)
C(44)	560(2)	3418(4)	1942(2)
C(38)	1016(2)	3518(4)	1448(2)

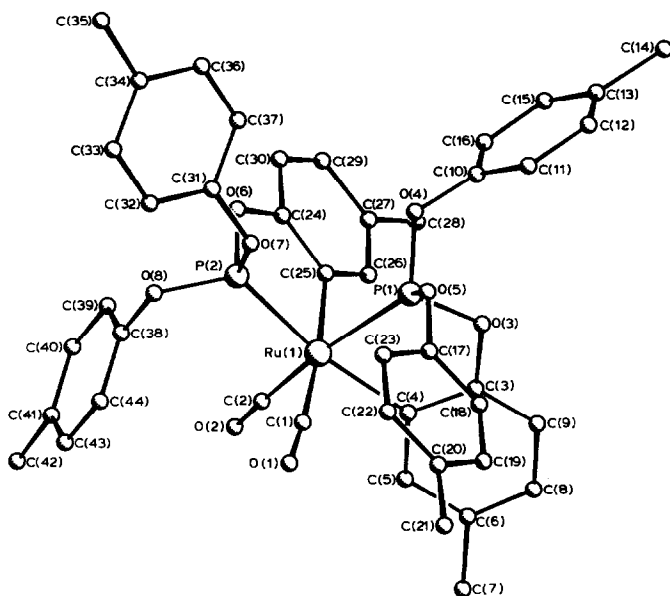


Fig. 2. A molecule of $\text{Ru}\{\text{P}(\text{OC}_6\text{H}_3\text{Me})(\text{OC}_6\text{H}_4\text{Me-4})_2\}_2(\text{CO})_2$ (**2b**), showing atom numbering scheme.

TABLE 2

SELECTED BOND DISTANCES AND ANGLES FOR $\text{Ru}\{\text{P}(\text{OC}_6\text{H}_3\text{Me})(\text{OC}_6\text{H}_4\text{Me-4})_2\}_2(\text{CO})_2$ (**2b**) AND $\text{Ru}\{\text{P}(\text{OC}_6\text{H}_4)(\text{OPh})_2\}_2\{\text{P}(\text{OPh})_3\}_2$ (**5**)

	2b ^a	5 ^b
<i>Bond distances (Å)</i>		
Ru–P(1)	2.272(2)	2.264(2)
Ru–C(4)	2.155(7)	2.156(8)
Ru–P(2)	2.258(2)	2.245(3)
Ru–C(25)	2.146(6)	2.125(7)
Ru–L(1)	1.937(7)	2.288(2)
Ru–L(2)	1.936(8)	2.312(2)
<i>Bond angles (deg)</i>		
P(1)–Ru–P(2)	93.4(1)	90.7(1)
P(1)–Ru–C(4)	78.5(2)	77.5(2)
P(1)–Ru–C(25)	83.5(2)	84.2(2)
P(1)–Ru–L(1)	98.7(2)	97.3(1)
P(1)–Ru–L(2)	160.0(2)	163.6(1)
P(2)–Ru–C(4)	170.6(2)	164.4(2)
P(2)–Ru–C(25)	79.2(2)	79.2(2)
P(2)–Ru–L(1)	95.9(2)	105.9(1)
P(2)–Ru–L(2)	99.0(2)	93.9(1)
C(4)–Ru–C(25)	95.1(2)	89.4(3)
C(4)–Ru–L(1)	90.1(3)	85.9(2)
C(4)–Ru–L(2)	87.6(3)	94.8(2)
C(25)–Ru–L(1)	174.7(3)	174.6(2)
C(25)–Ru–L(2)	83.4(3)	81.2(2)
L(1)–Ru–L(2)	95.7(3)	96.6(1)

^a This work. ^b Ref. 5.

thermal parameters were introduced for all non-hydrogen atoms and a weighting scheme, $w = k/[\sigma^2(F) + |g|F^2]$, included. The refinement converged with final $R = 0.051$ and $R_w = 0.057$ (for k 4.56 and g 0.0005). Hydrogen atoms were not included in the model. The analysis of variance showed no special features and the maximum residual electron density peak in the final difference map was $0.68 \text{ e}\text{\AA}^{-3}$ located in the vicinity of a phenyl group. Neutral scattering factors for Ru (and values of $\Delta f'$ and $\Delta f''$) were from ref. [9] and those for the remaining atoms were those incorporated in SHELX [8].

The fractional atomic coordinates are listed in Table 1 and a molecule of **2b** with the numbering scheme used is shown in Fig. 2. Selected interatomic parameters are given in Table 2*.

Results and discussion

The structure comprises discrete molecular units of **2b**; there are no significant intermolecular contacts less than those expected from Van der Waals radii. The six-coordinate Ru atom exists in a distorted octahedral environment comprised of *cis*-carbonyl groups and two *ortho*-metallated tri-*p*-tolyl phosphite ligands which form planar, five-membered rings. The P atoms occupy approximate *cis* positions in the Ru atom environment (Ru–P 2.258(2), 2.272(2) Å; P(1)–Ru–P(2) 93.4(1)° and C(4)–Ru–C(25) 95.1(2)°). The greatest deviation from ideal octahedral geometry is found in the angle of 160.0(2)° for P(1)–Ru–C(2) which can be related to the restricted bite distance of the *ortho*-metallated phosphite ligand. The Ru–C(aryl) bond distances (2.146(6), 2.155(7) Å) are approximately 0.2 Å longer than the Ru–C(carbonyl) bonds (1.936(8), 1.937(7) Å). As has been noted earlier [5] the angles about the P atom are reduced on *ortho*-metallation. The contraction of the P–O–C angles illustrates this point best: in the *ortho*-metallated phosphites the P–O–C(C₆H₃Me) angles of ca. 115° are significantly less (5–10°) than the corresponding angles for the other non-metallated tolyloxy groups.

Except for the obvious differences due to the substitution of the monodentate phosphite ligands in **5** for the carbonyls in **2b**, the comparable bond distances in both structures are equal within experimental error (Table 2). In addition, the angles subtended at the Ru atoms by the *ortho*-metallated phosphite ligands in both complexes are virtually identical (average angle P–Ru–C 78.6(1)°) as are the angles subtended at the Ru by the monodentate ligands i.e. 95.7(3)° for C(1)–Ru–C(2) in **2b** and 96.6(1)° for P(1)–Ru–P(4) in **5**. The largest difference found in the angles about the Ru atoms in **2b** and **5** is found for P(2)–Ru–C(1), 95.9(2)° in **2b** compared with 105.9(1)° for the equivalent P(2)–Ru–P(4) in **5**, undoubtedly reflecting the decreased steric strain in **2b** as would be expected on replacement of two relatively bulky P(OAr)₃ ligands by two linear CO groups.

In conclusion, the coordination geometries of the *ortho*-metallated phosphite ligands in **2b** and **5** are remarkably similar, there being no significant alteration in the geometries of the two complexes when CO is replaced by P(OPh)₃. The

* The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

formation of complexes of type **2** in the pyrolysis of **1** ($R = Me$) requires a migration of one of the tertiary phosphite ligands from one metal to a second already bearing such a ligand; the phosphite-free ruthenium carbonyl fragment is incorporated in the tetranuclear cluster **4**. That either the migration is not stereospecific or that ready isomerisation of complexes of type **2** may occur is shown by the formation of two isomers of **2c** in the pyrolysis of **1** ($R = H$) [1].

Acknowledgements

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