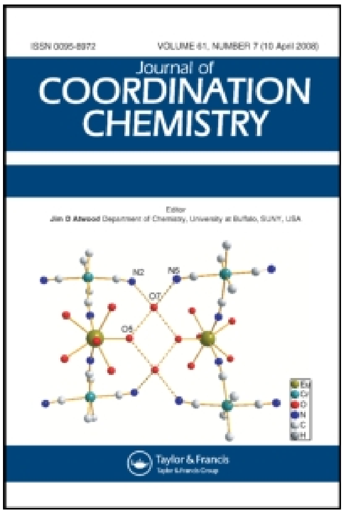

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SYNTHESIS, CHARACTERIZATION, AND X-RAY STRUCTURE OF BISfn-ACETATO DICARBONYL(DI-*TERI*-BUTYLPHOSPHINE) RUTHENIUM (I)]

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SYNTHESIS, CHARACTERIZATION, AND X-RAY STRUCTURE OF BIS[μ-ACETATO DICARBONYL(DI-*TERT*-BUTYLPHOSPHINE) RUTHENIUM (I)]

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$Ru_3(CO)_{12}$ reacts with di-*tert*-butylphosphine and acetic acid in di-*n*-butylether under reflux to form bis[μ-acetatodicarbonyl(di-*tert*-butylphosphine)ruthenium (I)] (**1**) in 80% yield. The crystal structure of **1** has been determined by single crystal X-ray diffraction methods. Crystal data for **1**: $C_{24}H_{42}O_8P_2Ru_2$, M = 722.7, orthorhombic, space group *Pbca*, a = 12.955 (2), b = 17.347 (2), c = 28.638 (4) Å, U = 6435.8 (5) Å^3, D_c = 1.492 gcm^{-3}, λ(Mo Kα) = 0.71073 Å, graphite monochromator, μ = 10.56 cm^{-1}. Methods: MULTAN, difference Fourier, full-matrix least-squares. Refinement of 2298 reflections ($I > 3\sigma(I)$) out of 6288 unique observed ($3° < 2\theta < 50°$) gave R and R_w values of 0.050 and 0.057, respectively. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were not located. Data/parameter ratio = 7.07, shift to error ratio = 0.38, highest peak in the final difference Fourier = 0.70 Å^{-3}. Data were collected on an Enraf-Nonius CAD-4 diffractometer at 23 ± 2° C. The complex has a Ru–Ru bond of 2.735 (1) Å which is bridged by two *cis* acetate groups. The CO groups also occupy *cis* locations on each Ru, while the two *t*-Bu_2PH ligands occupy axial positions *trans* to the metal–metal bond. The coordination geometry about each Ru atom is roughly octahedral. The overall geometry of the molecule can be described as that of a "sawhorse-like" structure.

Keywords: Ruthenium (I), phosphine, dinuclear complex, acetate, carbonyl, X-ray structure

INTRODUCTION

As part of a study of the reactions of secondary phosphines (R_2PH) with transition metal carbonyl complexes, we have investigated the reaction of $Ru_3(CO)_{12}$ with di-*tert*-butylphosphine (*t*-Bu_2PH) under forcing conditions (refluxing di-*n*-butyl ether).[1] These reactions result in cleavage of P–H and P–C bonds to give a variety of phosphido and phosphinidene complexes such as $Ru_3(\mu\text{-}H)_2(t\text{-}Bu_2P)_2(CO)_8$ and $Ru_3(\mu\text{-}H)_2(t\text{-}Bu_2PH)(\mu_3\text{-}t\text{-}BuP)(CO)_8$.[1] The reaction of $Ru_3(CO)_{12}$ with tertiary phosphines such as tri-*tert*-butylphosphine and a variety of organic acids results in breakdown of the Ru_3 core and formation of dinuclear bis(μ-acetato)carbonyl phosphine complexes of the type bis[μ-carboxylatodicarbonyl(phosphine)ruthenium(I)] (Ru–Ru).[2] We therefore investigated the reaction of $Ru_3(CO)_{12}$ with *t*-Bu_2PH and acetic acid with the expectation that a phosphido or phosphinidene acetato complex would be formed. However, in refluxing di-*n*-butyl ether, the dinuclear bis-acetato bridged phosphine complex $[Ru(\mu\text{-}O_2CMe)(CO)_2(t\text{-}Bu_2PH)]_2$ (**1**) is formed in 81% yield. This paper describes the synthesis, characterization, and X-ray crystal structure of **1**.

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TABLE I

Crystal Structure Parameters for Complex **1**.

Description of Crystal	**(1)**
Colour	yellow
Habit	prism
Max. crystal dimension (mm)	0.15 × 0.23 × 0.21
Crystal system	orthorhombic
Space group	*Pbca*
Unit cell parameters:	
a (Å)	12.955 (2)
b (Å)	17.347 (2)
c (Å)	28.638 (4)
U (Å^3)	6435.8
Molecules per unit cell	8
Formula	$C_{24}H_{44}O_8P_2Ru_2$
Molecular weight (g mol^{-1})	724.69
Calculated density (g cm^{-3})	1.49
μ-calc. (cm^{-1})	10.56
Data Collection	
Radiation (Å)	Mo Kα (0.71073)
Scan technique	θ/2θ
Scan width (deg)	0.55 + 0.35 (tan θ)
Range of indices h, k, l	+ 12, + 20, + 33
2θ range (deg)	3.0 to 50.0
No. reflections measured	6288
Standard reflections	
intensity	5 7 4, 3 0 14
orientation	4 8 5, 5 $\bar{7}$ 4
Decay of standards	−2.1%
Min. % transmission	84.8
Max. % transmission	98.4
Average % transmission	90.5
Structure Determination	
No. reflections used ($I > 3\sigma(I)$)	2298
No. parameters varied	325
Data/parameter ratio	7.071
Shift to error ratio	0.385
E.s.d. of an observation of unit weight	3.187
R^a	0.050
$R_w{}^a$	0.057

[a] R and R_w are defined as $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|^2]^{1/2}$.

RESULTS AND DISCUSSION

The reaction of $Ru_3(CO)_{12}$ with di-*tert*-butylphosphine and acetic acid in refluxing di-*n*-butyl ether results in a lemon yellow solution after *ca* 24 h. From this solution, yellow crystals of **1** may be isolated following evaporation to dryness and recrystallization of the residue from hexane. The complex is air stable in the solid state and in

TABLE II

Selected bond distances (Å) for **1**.

Atom 1	Atom 2	Distance[a]
Ru1	Ru2	2.735(1)
Ru1	P1	2.465(4)
Ru1	O6	2.12(1)
Ru1	O7	2.10(1)
Ru1	C1	1.82(1)
Ru1	C2	1.80(2)
Ru2	P2	2.458(5)
Ru2	O5	2.11(1)
Ru2	O8	2.10(1)
Ru2	C3	1.79(2)
Ru2	C4	1.82(2)
P1	C11	1.89(1)
P1	C15	1.89(1)
P2	C21	1.83(1)
P2	C25	1.87(1)

[a] Numbers in parentheses are estimated standard deviations.

TABLE III

Selected bond angles (deg) for **1**.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O5	Ru2	C3	94.6(6)	Ru2	Ru1	P1	162.0(1)
O5	Ru2	C4	176.7(6)	Ru2	Ru1	O6	82.2(3)
O8	Ru2	C3	175.9(6)	Ru2	Ru1	O7	83.1(3)
O8	Ru2	C4	95.7(6)	Ru2	Ru1	C1	95.6(5)
C3	Ru2	C4	86.7(8)	Ru2	Ru1	C2	93.2(5)
Ru1	P1	C11	119.9(5)	P1	Ru1	O6	84.6(3)
Ru1	P1	C15	117.4(5)	P1	Ru1	O7	83.2(3)
C11	P1	C15	111.6(7)	P1	Ru1	C1	97.8(5)
Ru2	P2	C21	119.6(5)	P1	Ru1	C2	99.0(5)
Ru2	P2	C25	118.7(6)	O6	Ru1	O7	82.8(4)
C21	P2	C25	116.8(7)	O6	Ru1	C1	95.7(6)
Ru2	O5	C5	124.2(9)	O6	Ru1	C2	174.1(6)
Ru1	O6	C5	125.6(9)	O7	Ru1	C1	178.1(6)
Ru1	O7	C7	124.8(9)	O7	Ru1	C2	93.0(6)
Ru2	O8	C7	125.6(9)	C1	Ru1	C2	88.5(7)
Ru1	C1	O1	178 (1)	Ru1	Ru2	P2	162.4(2)
Ru1	C2	O2	178 (2)	Ru1	Ru2	O5	83.3(3)
Ru2	C3	O3	178 (2)	Ru1	Ru2	O8	82.2(3)
Ru2	C4	O4	178 (2)	Ru1	Ru2	C3	94.3(5)
				Ru1	Ru2	C4	93.6(5)

Numbers in parentheses are estimated standard deviations.

solution for several hours. Spectroscopic data for **1** is in accord with the structure as determined by X-ray crystallography. Thus, the ^{1}H NMR spectrum contains resonances assigned to the phosphine and acetate units and the $^{31}P\{^{1}H\}$ NMR shows a singlet at (δ 37.43) which splits into a doublet ($^{1}J_{P\text{-}H} = 389.4$ Hz) in the ^{31}P spectrum. The IR spectrum shows a weak $\upsilon_{P\text{-}H}$ peak at 2324 cm^{-1}.

The compound **1** crystallizes in the orthorhombic space group *Pbca* (No. 61) with eight molecules per unit cell. Relevant crystal structure parameters are given in Table I and bond lengths and angles in Tables II and III. Positional parameters are given in Table IV.

TABLE IV

Positional Parameters for **1**.

Atom	*x/a*	*y/b*	*z/c*	B(Å^2)
Ru1	0.71558(9)	0.16868(6)	0.16764(4)	3.30(2)
Ru2	0.7197(1)	0.09625(6)	0.08285(4)	3.64(2)
P1	0.7705(4)	0.2276(2)	0.2419(1)	4.10(8)
P2	0.7806(6)	0.0327(2)	0.0113(1)	7.0(1)
O1	0.560(1)	0.2855(7)	0.1390(5)	7.9(3)
O2	0.543(1)	0.0723(7)	0.2015(5)	8.4(4)
O3	0.559(1)	0.1969(7)	0.0424(4)	8.4(4)
O4	0.550(1)	−0.0128(8)	0.1079(5)	9.4(4)
O5	0.8421(8)	0.1738(5)	0.0695(3)	5.2(2)
O6	0.8443(8)	0.2279(5)	0.1391(3)	4.9(2)
O7	0.8283(8)	0.0861(5)	0.1847(3)	4.9(2)
O8	0.8370(8)	0.0319(5)	0.1153(3)	4.4(2)
C1	0.620(1)	0.2410(9)	0.1510(5)	4.6(4)
C2	0.612(1)	0.110(1)	0.1891(5)	5.7(4)
C3	0.623(1)	0.157(1)	0.0576(5)	6.2(4)
C4	0.616(1)	0.0305(9)	0.0979(6)	6.0(4)
C5	0.880(1)	0.2186(7)	0.0993(5)	3.6(3)
C6	0.976(1)	0.264(1)	0.0868(6)	5.8(4)
C7	0.869(1)	0.0412(7)	0.1566(5)	3.6(3)
C8	0.960(1)	−0.0061(9)	0.1709(6)	4.7(4)
C11	0.772(1)	0.3363(7)	0.2484(5)	4.8(3)
C12	0.798(2)	0.3681(8)	0.2005(6)	7.4(5)
C13	0.855(2)	0.363(1)	0.2836(7)	8.5(5)
C14	0.665(2)	0.367(1)	0.2630(8)	8.1(6)
C15	0.729(1)	0.1786(8)	0.2977(5)	5.1(4)
C16	0.781(2)	0.209(1)	0.3410(6)	10.2(7)
C17	0.757(2)	0.0926(9)	0.2910(5)	6.7(5)
C18	0.609(1)	0.184(1)	0.3016(6)	7.0(5)
C21	0.785(2)	0.0870(8)	−0.0436(4)	5.7(4)
C22	0.808(3)	0.167(1)	−0.0354(6)	14(1)
C23	0.854(2)	0.058(1)	−0.0794(8)	15.8(9)
C24	0.677(2)	0.089(1)	−0.0629(9)	13.6(8)
C25	0.769(2)	−0.0747(8)	0.0065(6)	6.4(4)
C26	0.778(2)	−0.1103(9)	0.0521(6)	9.4(6)
C27	0.831(2)	−0.111(1)	−0.0319(8)	12.6(8)
C28	0.654(2)	−0.091(1)	−0.009(1)	12.1(7)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3* [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)].

A view of the molecule is shown in Figure 1. The overall geometry of the molecule is similar to that found in $[Ru(\mu\text{-}O_2CC_3H_7)(CO)_2(t\text{-}Bu_3P)]_2$. The geometry can be described as a "sawhorse" with *cis* bridging acetato units and *cis* CO ligands on each Ru atom. The phosphine ligands occupy axial positions *trans* to the Ru–Ru bond.

The Ru–Ru distance in **1** is 2.735 (1) Å which is within the range expected for a Ru–Ru single bond.[3] It is similar to that found in $[Ru(\mu\text{-}O_2CC_3H_7)(CO)_2(t\text{-}Bu_3P]_2$ (2.728 (1) Å)[4] and the related amine complex $[Ru(\mu\text{-}O_2CMe)(CO)_2(C_5H_5N)]_2$ (2.678 (1) Å).[5] The μ-acetato bridges, CO, and phosphine ligands give each Ru atom a roughly octahedral coordination geometry. There is some distortion from an idealized geometry as evidenced by Ru(1)–Ru(2)–P(2) and Ru(2)–Ru(1)–P(1) angles of 162.4 (2)° and 162.0 (1)° respectively. In addition, the Ru–P distances of 2.465 (4) and 2.458 (5) Å for Ru(1)–P(1) and Ru(2)–P(2) are notably shorter than those found in the tri-*t*-butylphosphine(μ-n-butyrato)complex $[Ru(\mu\text{-}O_2CC_3H_7)(CO)_2(t\text{-}Bu_3P)]_2$ (2.619 (3) Å and 2.627 (3) Å).[4] It seems likely that the exceptionally long Ru–P distances in the latter compound are due to steric effects caused by the bulky $t\text{-}Bu_3P$ ligands. The P–H atoms of the $t\text{-}Bu_2PH$ groups were not located in the X-ray structure. Their presence, however, is inferred from spectroscopic data.

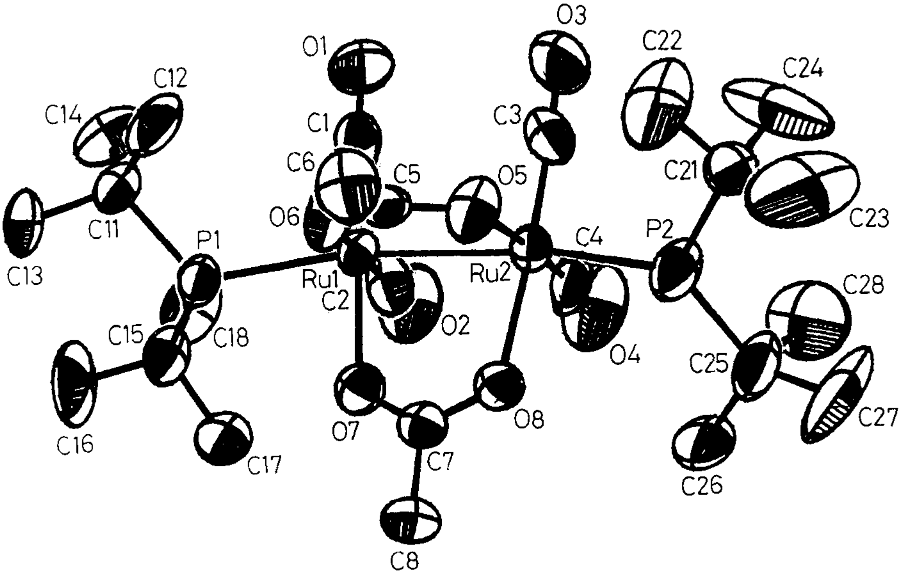

FIGURE 1 ORTEP diagram of **1** showing the atom numbering scheme.

EXPERIMENTAL

General

All reactions were performed under oxygen-free nitrogen or under vacuum. Hexane was dried over sodium/benzophenone and distilled under nitrogen before use. Di-*n*-butyl ether was dried over KOH and distilled under nitrogen. $Ru_3(CO)_{12}$[6] and $t\text{-}Bu_2PH$[7] were prepared by literature methods. Acetic acid (glacial, 17.4 M) was used as received from American Scientific Products.

Instruments

NMR: GE QE-300 (^1H, ^{31}P), IR: Digilab FTS-40. NMR spectra were recorded in C_6D_6 at ambient temperature and are referred to Me_4Si, (^1H), and 85% H_3PO_4 (^{31}P) (δ 0.0). Melting points were measured in sealed capillaries under nitrogen (1 atm) and are uncorrected.

Preparation of $Ru_2(\mu\text{-}O_2CMe)_2(CO)_2(t\text{-}Bu_2PH)_2$ (**1**)

Excess acetic acid (1 cm^3, 17.5 mmol) was added to a solution of $Ru_3(CO)_{12}$ (0.20 g, 0.33 mmol) and di-*tert*-butylphosphine (0.10 cm^3, 0.73 mmol) in di-*n*-butyl ether (50 cm^3). The mixture was stirred and heated under reflux for 24 hours. During this time the solution turned from orange to lemon yellow. The solution was cooled to room temperature, and volatile materials were removed under vacuum. The residue was extracted into hexane (50 cm^3), and resulting yellow solution was evaporated under vacuum (35 cm^3). Cooling (−40° C) gave yellow crystals of **1** which were collected and dried under vacuum. Yield: 0.21 g (81%), mp: 212–214° C. IR: (nujol mull, NaCl), 2324 w, 2318 w, 2019 s, 1965 s, 1936 s, 1907 m, 1884 w, 1583 s, 1556 w, 1531 w, 1109 w, 1198 w, 1185 m, 1047 w, 1024 m, 959 w, 875 w, 814 w, 792 m, 688 w, 566 w, 534 w (cm^{-1}). NMR: ^1H: δ 3.94 (d, 2H, $t\mathrm{Bu_2P}\text{-}H$, $^1J_{P\text{-}H}$ = 309.8 Hz); δ 1.73, (s, 6H, O_2CMe); δ 1.30, (d, 36H, $t\text{-}Bu_2\mathrm{PH}$, $^2J_{P\text{-}H}$ = 11.1 Hz; $^{31}P\{^1H\}$: δ 37.43 (s); ^{31}P: the δ 37.43 peak splits into a doublet, $^1J_{P\text{-}H}$ = 289.4 Hz.

X-ray Experimental

Crystals of **1** were mounted in thin glass capillaries under a nitrogen atmosphere. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. Final lattice parameters were determined from the angular settings of 25 strong reflections ($22° < 2\theta < 28°$). Data were collected by the $\theta/2\theta$ scan technique at 23 ± 2° C. Details of the standard data collection methods were similar to those outlined previously.[8] All calculations were performed on a PDP 11/44 computer using the Enraf-Nonius CAD-4 software package "SDP-PLUS".[9]

The orthorhombic space group *Pbca* was uniquely determined by the systematic absences ($h0l$, $l = 2n + 1$, $0kl$, $k = 2n + 1$, $hk0$, $h = 2n + 1$). Data were collected in the $+h$, $+k$, $+l$ quadrant between 2θ values of 3.0 and 50.0°. The data were then corrected for Lorentz and polarization effects. The check reflections showed a 2.1% decrease in intensity over the course of data collection. An anisotropic decay correction was therefore applied. A Ψ scan of 4 reflections having χ values between 80° and 90° showed a minimum percent transmission of 84.8 and a maximum percent transmission of 98.4. An empirical absorption correction (Program EAC) was applied. The positions of the heavy atoms were obtained by direct methods (MULTAN),[10] and the remaining non-hydrogen atoms were located by successive cycles of difference Fourier maps followed by least-squares refinement. No hydrogen atoms were located, and data with intensities less than $3\sigma(I)$ and $\sin\theta/\lambda$ less than 0.10 were excluded. A non-Poisson contribution weighting scheme with an instability factor *P*, set at 0.06, was used in the final stages of refinement.[11] The structure was refined to final values of 0.050 and 0.057 for *R* and R_w, respectively. The highest peak in the final difference Fourier map had a height of 0.70 e/Å^3 and was located 1.01 Å from P(2). Scattering factors were taken from reference 12.

ACKNOWLEDGEMENTS

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SUPPLEMENTARY MATERIAL

Complete tables of bond lengths and angles, tables of thermal parameters, and observed and calculated structure factor tables for **1** (17 pages) have been deposited with the Editor and are available upon request.

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