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X-ray crystal structure determination of $(PhCOO)_2(PPh_3)_2(CO)_2Ru$. Stereochemistry assignments

M. Rotem, Z. Stein and Y. Shvo *

School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, 69978 Tel Aviv (Israel)

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Abstract

The complexes $(PhCOO)_2(PPh_3)_2(CO)_2Ru$ (**1**) and $(p\text{-}MeC_6H_4COO)_2$-$(PPh_3)_2(CO)_2Ru$ (**2**) have been made by treating tricarbonylbis(triphenylphosphine)ruthenium(0) with benzoic and *p*-toluic acid, respectively. An X-ray diffraction study of **1** has revealed an octahedral geometry with *trans* disposition of the phosphine ligands and *cis* disposition of the carbonyl ligands. The same stereochemistry is assigned to complex **2** and to several related complexes previously reported. This stereochemical assignment clarifies some conflicting statements in the literature.

Introduction

Metal carboxylate complexes are widespread in organo-transition metal chemistry. Their importance in catalysis has recently been demonstrated [1,2]. Of particular importance are the chiral 2,2′-bis(diphenylphosphino)-1,1′-binaphthylruthenium carboxylate (BINAP) complexes, recently discovered by Noyori et al. [3,4].

In connection with another study we found it necessary to establish the stereochemistry of complexes of the type $Ru(ArCOO)_2(CO)_2(PPh_3)_2$ where Ar = phenyl (**1**) and *p*-tolyl (**2**). A survey of the literature revealed that there was some confusion about the stereochemistry of complexes of this type and we have clarified the situation by an unambiguous X-ray structure determination of **1**.

d^6-Hexacoordinate complexes of the type $Ru(CO)_2L_2X_2$ (L = phosphine) can exist as the octahedral isomers with *cis* CO ligands **A**, **B** and **C**, and with *trans* CO ligands, **D** and **E**.

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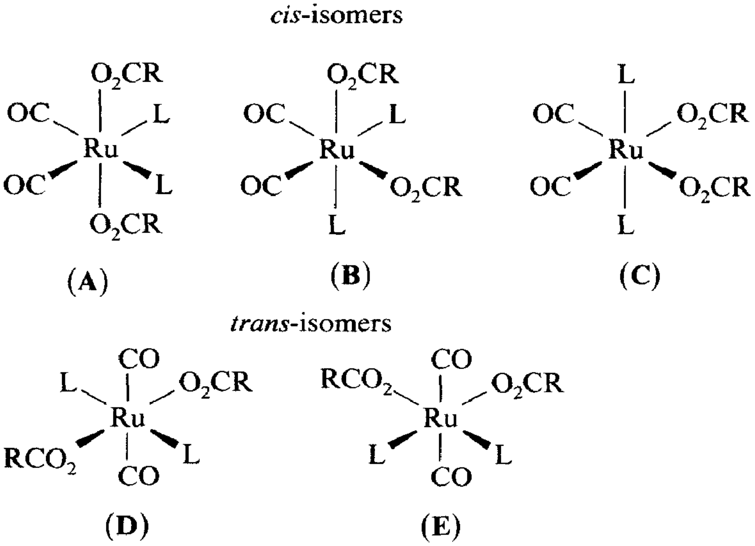


Scheme 1

Whereas the *trans* isomers are expected to exhibit a single strong infrared CO stretching vibration band, two bands are expected for the *cis* isomers. However, it is not a simple matter to distinguish among the isomers within each group by infrared spectroscopy unless all of the isomers are available. Configuration **A** was initially assigned [5] to a series of complexes of type **3**: $Ru(X)_2(CO)_2(PPh_3)_2$ (X = Cl, Br, I, CF_3CO_2). The configurational assignment was based on the similarity of the IR stretching frequencies (CO) with those of previously reported iso-structural dialkylphenylphosphine complexes [6]. The stereochemistry of the latter complexes was deduced from infrared and dipole moment measurements. A year later, NMR studies revealed that the complex $RuCl_2(CO)_2(PMe_2Ph)_2$ possess configuration **C**, with the phosphine ligands in a *trans* disposition [7]. Consequently, stereochemistry **C**, rather than **A** (Scheme 1), was proposed for the complexes of type **3**.

Several years later, being unaware of this correction, two research groups [8,9] still adopted configuration **A** for a series of new complexes of type **3**, where X = formate, acetate, propionate, *p*-chlorobenzoate, or *p*-nitrobenzoate. Later, becoming aware of the revision of the configuration, one of the group [10] allocated configuration **C** to several new perfluorocarboxylate complexes of type **3**.

Results and discussion

We have prepared the new complexes **1** and **2** by treating $Ru(CO)_3(PPh_3)_2$ [11] with benzoic and *p*-toluic acid, respectively, in a known procedure [9]. Infrared spectral data (Table 1) indicate that the carboxylates are unidentate (1610vs, 1350vs cm^{-1}) and that the CO ligands must be in a *cis* disposition (two CO stretching bands). The CO stretching frequencies are very similar to those reported for related complexes [8,9]. Most significant is the $^{13}CO-^{31}P$ spin coupling (t, ^2J 11.3 and 11.8 Hz (Table 2) for **1** and **2** respectively) which implies configuration **C** for the two complexes, since only form **C** has chemical as well as spin equivalent nuclei.

Table 1

Infrared and ^{1}H NMR spectroscopic data [a]

Compound	ν (cm^{-1})	^{1}H NMR (δ, ppm; J, Hz)
1	2045vs,1990vs,1960w,1610vs, 1573m,1490m,1440s,1350vs.	7.11(t, J 7.7, 2H), 7.47(d, J 7.7, 2H), 7.22(s, br 10H), 7.72(m, 6H) ^{31}P 25.66
2	2050vs,1990vs,1610vs,1570m, 1488m,1438s,1350vs.	2.30(s, 3H), 6.95(d, J 8, 2H), 7.52(d, J 8, 2H), 7.32(s, brd, 9H), 7.8(m, 6H). ^{31}P 25.02 [b]

[a] Infrared spectra were recorded with methylene chloride solutions on a Perkin Elmer grating spectrophotometer Model 177. NMR spectra were recorded with $CDCl_3$ solutions (TMS) on a Bruker FT-360 MHz spectrometer. The ^{31}P shifts are relative to H_3PO_4 (85%) as internal standard. [b] Measured in benzene-d_6.

Table 2

^{13}C NMR spectral data (δ, ppm)

	1	2
ArCOO		
C1	135.8s	140.5s
C2,6	129.2d	130.7d
C3,5	126.7d	128.1d
C4	129.5d	133.1s
COO	172.1s	172.6s
Me	–	21.9q
PPh		
C1	129.9(d, ^1J(P–C) 23.9 Hz)	131.6(d, ^1J(P–C) 23.5 Hz)
C2,6	134.1(dd, ^2J(P–C) 5.3 Hz)	135.1(t, brd.)
C3,5	128.2d	129.0d
C4	130.4	131.2d
CO	196.9(t, ^2J(P–C) 11.3 Hz)	197.5(t, ^2J(P–C) 11.8 Hz)

Table 3

Crystal data for $Ru(PhCO_2)_2$-$(CO)_2(PPh_3)_2$ (**1**)

M_r	923.9
Space group	$P2_1n$
Z	4
a (Å)	12.082(2)
b (Å)	18.810(7)
c (Å)	19.357(2)
α (°)	90.0
β (°)	102.27(1)
γ (°)	90.0
V (Å^3)	4298.63
d_c (g/cm^3)	1.428
μ(Mo-K_α) (cm^{-1})	4.8
2θ-limits (°)	46
Data with $I \geqslant 3\sigma(I)$	2672
R'	0.0535
R_w	0.0523

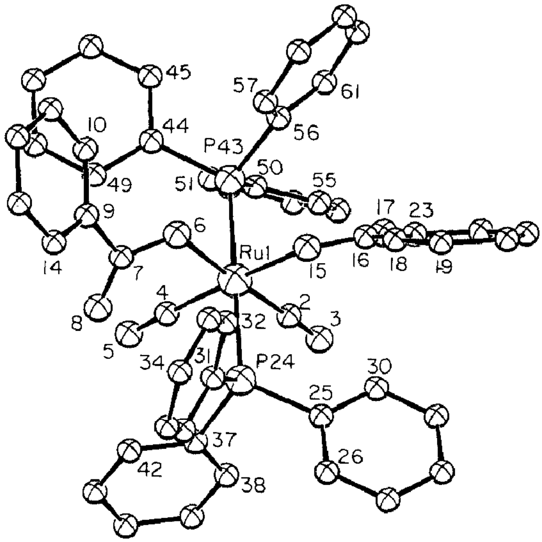


Fig. 1. ORTEP diagram of $(PhCOO)_2(PPh_3)_2(CO)_2Ru$ (**1**). Hydrogen atoms have been omitted for clarity.

The previous stereochemical uncertainty and the lack of structural X-ray data for this type of complexes prompted us to carry out an X-ray diffraction study of **1** (Fig. 1, Tables 3–5). This revealed a *cis* disposition of the CO ligands and a *trans* disposition of the two phosphines (structure **C**), in an octahedral geometry.

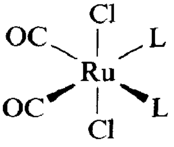
The similarity of the spectral data of **1** and **2** implies that they have identical stereochemistries. Furthermore, since **1** was prepared under conditions identical with those used for the iso-structural acetate, *p*-chlorobenzoate, and *p*-nitrobenzoate complexes [9], these must also possess the same stereochemistry as **1**, and so have structure **C**, not **A**.

For the following reasons, and in the light of experimental observations structure **C** is probably the most thermodynamically stable of the possible isomers.

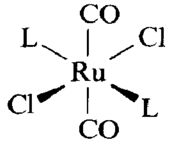
a. Being better π-acids than the other ligands, the two CO groups would tend to avoid a *trans* geometry that would destabilize structures **D** and **E** with respect to the others.

b. Being the most bulky ligands, the two triphenylphosphine groups would tend to adopt a *trans* geometry to minimize non-bonding interactions within the complex.

c. Chatt et al. [6] isolated two isomers of $RuCl_2(CO)_2(PR_3)_2$ to which structures **4** and **5** were assigned on the basis of infrared and dipole moment measurements. In accordance with earlier [7] as well as the present findings, the *cis* isomer probably posseses structure **6** and not **4**. Nevertheless, the *trans* isomer **5** was found [6] to be labile and to isomerize readily to the exceptionally chemically and thermally stable isomer **6**. This behavior lends further support to the view that the energy of the stereochemical arrangement in **C** is the lowest for all the isomers **A**–**E**.



(4)



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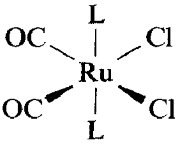

(6)

($L = PEt_2Ph$)

Experimental

Complexes **1** and **2** were obtained as yellow crystals by treating tricarbonylbis(triphenylphosphine)ruthenium with the appropriate aromatic carboxylic acid in the procedure described by Robinson and Uttley [9]. Complex **1** was recrystallized from a methylene chloride/cyclohexane mixture and a selected crystal was used for the X-ray study (Fig. 1, and Tables 3–5). Anal. Found: C, 67.49; H, 4.40. $C_{52}H_{40}O_6P_2Ru$ calcd.: C, 67.61; H, 4.33%.

X-ray diffraction data were measured at ca. 18°C on CADH diffractometer equipped with a graphite monochromator using Mo-K_α (λ 0.7107 Å) radiation. The

Table 4

Bond lengths (Å) and bond angles (°) in $Ru(PhCO_2)_2(CO)_2(PPh_3)_2$ (**1**)

(a) Bond lengths			
Ru1–C2	1.861(10)	C7–C9	1.500(13)
Ru1–C4	1.873(10)	O15–C16	1.285(11)
Ru1–O6	2.083(7)	C16–O17	1.253(13)
Ru1–O15	2.086(5)	C16–C18	1.512(11)
Ru1–P24	2.424(2)	P24–C25	1.834(5)
Ru1–P43	2.397(2)	P24–C31	1.810(6)
C2–O3	1.135(13)	P24–C37	1.814(6)
C4–O5	1.134(12)	P43–C44	1.814(7)
O6–C7	1.290(13)	P43–C50	1.821(6)
C7–O8	1.231(14)	P43–C56	1.812(7)
(b) Bond angles			
P24–Ru1–P43	177.5(1)	C16–C18–C23	119.6(7)
O15–Ru1–P43	91.8(2)	C16–C18–C19	120.2(6)
O15–Ru1–P24	86.2(2)	Ru1–P24–C37	109.9(2)
O6–Ru1–P43	83.7(2)	Ru1–P24–C31	116.8(2)
O6–Ru1–P24	94.4(2)	Ru1–P24–C25	116.5(2)
O6–Ru1–O15	81.0(2)	C31–P24–C37	107.7(3)
C4–Ru1–P43	91.9(3)	C25–P24–C37	103.7(3)
C4–Ru1–P24	89.9(3)	C25–P24–C31	101.1(3)
C4–Ru1–O15	174.9(4)	P24–C25–C30	121.7(4)
C4–Ru1–O6	95.9(4)	P24–C25–C26	118.2(4)
C2–Ru1–P43	92.6(3)	P24–C31–C36	117.5(5)
C2–Ru1–P24	89.2(3)	P24–C31–C32	122.3(4)
C2–Ru1–O15	97.1(4)	P24–C37–C42	121.9(4)
C2–Ru1–O6	175.8(4)	P24–C37–C38	117.4(4)
C2–Ru1–C4	86.1(5)	Ru1–P43–C56	113.9(2)
Ru1–C2–O3	175.7(9)	Ru1–P43–C50	112.2(2)
Ru1–C4–O5	175.0(10)	Ru1–P43–C44	117.4(2)
Ru1–O6–C7	121.5(7)	C50–P43–C56	106.8(3)
O6–C7–C9	112.8(9)	C44–P43–C56	102.0(3)
O6–C7–O8	126.6(10)	C44–P43–C50	103.3(3)
O8–C7–C9	120.5(10)	P43–C44–C49	122.0(5)
C7–C9–C14	120.6(7)	P43–C44–C45	117.6(5)
C7–C9–C10	119.3(7)	P43–C50–C55	120.3(4)
Ru1–O15–C16	124.1(6)	P43–C50–C51	119.6(4)
O15–C16–C18	115.7(9)	P43–C56–C61	117.0(5)
O15–C16–O17	124.0(9)	P43–C56–C57	122.8(4)
O17–C16–C18	120.0(9)		

Table 5

Atomic coordinates and thermal parameters for Ru(PhCO$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$ (**1**)

Atom	*x*	*y*	*z*	U_{eq} [a]
Ru1	0.1158(1)	0.2906(1)	0.2798(1)	0.0284(3)
C2	0.0451(9)	0.2106(6)	0.2338(5)	0.0385(32)
O3	0.0069(7)	0.1593(4)	0.2085(4)	0.0580(27)
C4	0.2165(10)	0.2269(6)	0.3351(5)	0.0428(32)
O5	0.2718(7)	0.1846(4)	0.3670(4)	0.0569(29)
O6	0.1837(6)	0.3819(4)	0.3334(3)	0.0359(23)
C7	0.2903(10)	0.3869(6)	0.3614(5)	0.0384(31)
O8	0.3643(6)	0.3432(4)	0.3569(4)	0.0529(27)
C9	0.3208(5)	0.4561(4)	0.3992(4)	0.0458(36)
C10	0.2523(5)	0.4825(4)	0.4430(4)	0.0549(38)
C11	0.2824(5)	0.5450(4)	0.4811(4)	0.0794(36)
C12	0.3808(5)	0.5812(4)	0.4754(4)	0.0821(40)
C13	0.4492(5)	0.5548(4)	0.4316(4)	0.0834(38)
C14	0.4192(5)	0.4922(4)	0.3935(4)	0.0499(33)
O15	0.0163(6)	0.3665(3)	0.2167(3)	0.0347(24)
C16	−0.0835(9)	0.3544(6)	0.1797(5)	0.0360(32)
O17	−0.1410(6)	0.3005(4)	0.1867(4)	0.0550(26)
C18	−0.1258(5)	0.4065(4)	0.1205(3)	0.0378(30)
C19	−0.0607(5)	0.4657(4)	0.1115(3)	0.0505(33)
C20	−0.0959(5)	0.5106(4)	0.0536(3)	0.0628(36)
C21	−0.1963(5)	0.4964(4)	0.0049(3)	0.0714(32)
C22	−0.2615(5)	0.4373(4)	0.0140(3)	0.0675(37)
C23	−0.2262(5)	0.3923(4)	0.0718(3)	0.0589(34)
P24	0.2370(2)	0.2952(2)	0.1949(1)	0.0325(10)
C25	0.1675(4)	0.2838(4)	0.1017(3)	0.0360(29)
C26	0.2336(4)	0.2891(4)	0.0510(3)	0.0571(34)
C27	0.1836(4)	0.2821(4)	−0.0206(3)	0.0525(33)
C28	0.0675(4)	0.2697(4)	−0.0414(3)	0.0493(33)
C29	0.0013(4)	0.2643(4)	0.0093(3)	0.0523(33)
C30	0.0514(4)	0.2713(4)	0.0809(3)	0.0502(32)
C31	0.3146(5)	0.3769(3)	0.1911(3)	0.0330(31)
C32	0.4217(5)	0.3780(3)	0.1749(3)	0.0561(35)
C33	0.4746(5)	0.4427(3)	0.1680(3)	0.0640(38)
C34	0.4205(5)	0.5064(3)	0.1775(3)	0.0606(33)
C35	0.3134(5)	0.5053(3)	0.1938(3)	0.0607(35)
C36	0.2605(5)	0.4406(3)	0.2006(3)	0.0407(33)
C37	0.3389(4)	0.2231(3)	0.2113(3)	0.0320(30)
C38	0.3037(4)	0.1569(3)	0.1824(3)	0.0351(31)
C39	0.3724(4)	0.0973(3)	0.2011(3)	0.0502(34)
C40	0.4763(4)	0.1041(3)	0.2486(3)	0.0477(33)
C41	0.5114(4)	0.1703(3)	0.2775(3)	0.0508(34)
C42	0.4427(4)	0.2299(3)	0.2588(3)	0.0430(29)
P43	−0.0050(2)	0.2915(2)	0.3633(1)	0.0336(10)
C44	0.0605(4)	0.3087(4)	0.4551(4)	0.0325(29)
C45	−0.0109(4)	0.3229(4)	0.5014(4)	0.0570(33)
C46	0.0337(4)	0.3283(4)	0.5739(4)	0.0716(36)
C47	0.1497(4)	0.3195(4)	0.6000(4)	0.0705(33)
C48	0.2211(4)	0.3053(4)	0.5537(4)	0.0543(34)
C49	0.1765(4)	0.2999(4)	0.4813(4)	0.0390(28)
C50	−0.0759(5)	0.2066(3)	0.3669(3)	0.0359(30)
C51	−0.1546(5)	0.1828(3)	0.3079(3)	0.0408(30)
C52	−0.2054(5)	0.1164(3)	0.3091(3)	0.0471(34)
C53	−0.1774(5)	0.0737(3)	0.3692(3)	0.0528(33)

Table 5 (continued)

Atom	x	y	z	U_{eq} [a]
C54	−0.0987(5)	0.0974(3)	0.4281(3)	0.0567(33)
C55	−0.0479(5)	0.1639(3)	0.4270(3)	0.0403(29)
C56	−0.1147(6)	0.3588(3)	0.3459(3)	0.0398(30)
C57	−0.2293(6)	0.3431(3)	0.3396(3)	0.0415(31)
C58	−0.3088(6)	0.3979(3)	0.3309(3)	0.0582(33)
C59	−0.2738(6)	0.4684(3)	0.3285(3)	0.0598(37)
C60	−0.1592(6)	0.4840(3)	0.3349(3)	0.0667(34)
C61	−0.0796(6)	0.4292(3)	0.3436(3)	0.0474(35)

[a] U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor.

intensities of the reflections were collected by ω–2θ scan technique with scan range of $1.0 + 0.3 \tan \theta°$. All data were recorded at a constant 4° $\min^{-1}$ scan rate. The crystal used for data collection was a $0.2 \times 0.2 \times 0.3$ mm in size. The possible deterioration of the crystal was checked by recording frequently the intensities of three standard reflections, and was found negligible. An empirical method was applied to correct the data for adsorption [12].

The structure was solved by a combination of direct methods and Fourier techniques (MULTAN80). The refinement was carried out by large-block least-squares (SHELX) for the atomic coordinates and anisotropic thermal parameters of all nonhydrogen atoms. All H atoms were placed in calculated positions and assigned fixed isotropic temperature factors. The atomic coordinates of the hydrogen atoms were not refined. The phenyl groups were treated as geometrically constrained rigid groups, with ring bond lengths and angles of 1.395 Å and 120°, respectively. The final difference Fourier map showed no indications of incorrectly placed or missing atoms.

References

1 A. Dobson and S.D. Robinson, Inorg. Chem, 16 (1977) 137.
2 M. Rotem and Y. Shvo, Organometallics, 2 (1983) 1689.
3 R. Noyori, Chimica, 42 (1988) 215.
4 T. Ohata, H. Takaya and R. Noyori, Inorg. Chem., 27 (1988) 566.
5 J.P. Collman and W.R. Roper, J. Am. Chem. Soc., 87 (1965) 4008.
6 J. Chatt, B.L. Shaw and A.E. Field, J. Chem. Soc., (1964) 3466.
7 J.P. Collman and W.R. Roper, J. Am. Chem. Soc., 88 (1966) 3504.
8 B.F.G. Johnson, R.D. Johnston, and J. Lewis, J. Chem. Soc. A, (1971) 689.
9 S.D. Robinson and M.F. Uttley, J. Chem. Soc., Dalton, (1973) 1912.
10 A. Dobson and S.D. Robinson, Inorg. Chem., 16 (1977) 1321.
11 F. Piacenli, J. Inorg. Nucl. Chem., 29 (1967) 1389.
12 N. Walker, D. Stuart, Acta Crystallogr. Sect. A, 39 (1983) 158.