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Structural characterization and comparison of $[\text{Ru}_2(\text{O}_2\text{CR})_2(\text{CO})_4\text{L}_2]$

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Abstract

The structures of $[\text{Ru}_2(\text{CO})_4(\text{O}_2\text{CR})_2(\text{PPh}_3)_2]$ ($\text{R} = \text{Me}$ (1), Ph (2), and CF_3 (3)) have been determined by X-ray crystallography: 1, monoclinic, $C2/c$, $a = 24.630(8)$, $b = 9.2476(21)$, $c = 18.735(4)$ Å, $\beta = 101.710(20)^\circ$, $Z = 4$, $R = 0.026$, $R_w = 0.025$, based on 3243 reflections with $I > 2\sigma(I)$; 2, orthorhombic, $P2_12_12_1$, $a = 12.590(3)$, $b = 18.188(3)$, $c = 20.804(5)$ Å, $Z = 4$, $R = 0.033$, $R_w = 0.026$, based on 3410 reflections with $I > 2\sigma(I)$; 3, triclinic, $P\bar{1}$, $a = 12.7329(19)$, $b = 13.450(4)$, $c = 13.7939(20)$ Å, $a = 76.770(16)$, $\beta = 73.305(14)$, $\gamma = 76.017(16)^\circ$, $Z = 2$, $R = 0.054$, $R_w = 0.047$, based on 5543 reflections with $I > 2\sigma(I)$. The Ru–Ru bond lengths are 2.7360(9) Å in 1, 2.7411(8) Å in 2, and 2.7276(9) Å in 3. Comparison of these structures with those of other dinuclear Ru^I structures of the general formula $[\text{Ru}_2(\text{O}_2\text{CR})_2(\text{CO})_4\text{L}_2]$ ($\text{L} = \text{CO}$, PPh_3 , PBu_3 , py , H_2O , or PhCO_2H ; $\text{R} = \text{Me}$, CF_3 , ^iPr , or $4\text{-FC}_6\text{H}_4$) or of $[\text{Ru}_2(\text{O}_2\text{CPh})_2(\text{CO})_4]_n$ reported to date leads to the conclusion that the axial ligand is the most influential in determining the length of the Ru–Ru single bond, and that the equatorial ligand is responsible for the secondary effect.

1. Introduction

Our recent interest in exploring the unusual physical and chemical influences of multidentate ligands on the transition-metal carbonyl derivatives of the ligands [1] has led us to investigate the influence of bidentate ligands such as carboxylates in dinuclear carbonyl complexes. Since the complexes such as $[\text{Ru}_2(\text{O}_2\text{CR})_2(\text{CO})_4\text{L}_2]$ can be viewed as possible intermediates interconverting for the low- and high-valent cluster compounds (LVCs and HVCs), defined in 1983 by Cotton [2], research in this direction might identify new synthetic routes connecting the numerous LVCs such as $[\text{Ru}_3(\text{CO})_{12}]$ [3] and the well-established, multiply bonded dimers such as $[\text{Ru}_2(\text{O}_2\text{CR})_4\text{Cl}]$ [4]. In this paper, we present the structural details of $[\text{Ru}_2(\text{O}_2\text{CR})_2(\text{CO})_4(\text{PPh}_3)_2]$ ($\text{R} = \text{Me}$, Ph , or CF_3), compounds which are known to be important catalysts or catalytic precursors in reactions such as the hydroformylation of olefins or the addition of carboxylic acids to alkynes

[5–9], and we compare them with those of published dimers with different axial ligands, L, with L = pyridine (py) or CO [10,11]. Similar comparisons in HVCs such as $[\text{M}_2(\text{O}_2\text{CR})_4\text{L}_2]$ ($\text{M} = \text{Mo}$, Cr , or Rh) [12] have been reported in the literature. We hope that the comparison in $[\text{Ru}_2(\text{O}_2\text{CR})_2(\text{CO})_4\text{L}_2]$ can improve our understanding of the activation of the metal–metal multiply bonded dimers, the metal–metal bonds being maintained, and of the conversion from HVCs into LVCs.

2. Experimental section

Compounds, $[\text{Ru}_2(\text{O}_2\text{CR})_2(\text{CO})_4(\text{PPh}_3)_2]$ ($\text{R} = \text{Me}$, 1; Ph , 2; or CF_3 , 3), were prepared by the published procedure [9,13]. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of 1–3 in CDCl_3 were obtained at room temperature by a Bruker AMX-400 FT NMR spectrometer at 162 MHz with PPh_3 as an internal standard: 19.8, 21.7 and 21.3 ppm, respectively. Single crystals of 1–3 were grown from CH_2Cl_2 /hexane at room temperature. The pertinent crystal data are summarized in Table 1. The methods used have been presented elsewhere [14]. In 1, a C_2 axis is imposed crystallographically at the center of the

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Ru–Ru bond while in **3**, two CF₃ groups are disordered and eight fluorine atom positions with occupancy of 0.75 were found. All non-hydrogen atoms (excepting the fluorine atoms in **3**) were refined anisotropically. The final refinement converged smoothly and no chemically significant peaks were found in the final difference maps.

The fractional atomic coordinates of all the non-hydrogen atoms are listed in Table 2. Table 3 contains selected bond lengths and angles for **1–3**. Tables of the remaining bond lengths and angles, the hydrogen atomic coordinates, the anisotropic displacement coefficients, and structure factor (F_o vs. F_c) are available from the authors. The ORTEP plots for **1–3** are drawn in Figs. 1–3, respectively, with the relevant numbering scheme.

3. Results and discussion

As shown in Figs. 1–3, compounds **1–3** are quite similar, each adopting a sawhorse or *cis*-eclipsed struc-

ture, in which the two carbonyl groups on each metal are mutually *cis* and opposite the bridging groups, with the phosphine ligands in the axial sites opposite the Ru–Ru bond. This structural feature is similar to that reported for other bridged compounds, [Ru₂(O₂CR)₂(CO)₄L₂] with L = py, CO, P^tBu₃, H₂O, or PhCO₂H and R = Me, ⁿPr, 4-F-C₆H₄ or Ph [10,11,15,16] and [Ru₂X₂(CO)₄(PR₃)₂] with X⁻ = Cl⁻, 3,5-dimethylpyrazolato (Pz'⁻), or 2-oxypyridinato (NC₅H₄O⁻); R = Ph, ^tBu, or *p*-tol [17–19] but different from the *cis*-staggered structure observed for the unbridged dinuclear compound, [Ru₂(HBPz₃)₂(CO)₄] (Pz = pyrazolato) [20].

The Ru–Ru length is 2.7360(9) Å for **1**, 2.7411(8) Å for **2**, and 2.7276(9) Å for **3** (Table 3). The second value is the longest Ru–Ru distance so far seen in bridged Ru^I–Ru^I compounds [10,11,15–19], though that in the unbridged compound, [Ru₂(HBPz₃)₂(CO)₄] [20] is even longer (2.882(1) Å). In order to understand the possible factors influencing the variation in Ru–Ru

TABLE 1. Crystal data for **1–3**

compound	1	2	3
empirical formula	C ₄₄ H ₃₈ O ₈ P ₂ Ru ₂	C ₅₄ H ₄₀ O ₈ P ₂ Ru ₂	C ₄₄ H ₃₀ F ₆ O ₈ P ₂ Ru ₂
color	yellow	orange yellow	orange yellow
crystal size (mm)	0.40 × 0.40 × 0.45	0.30 × 0.40 × 0.40	0.40 × 0.40 × 0.30
space group	monoclinic, C2/c	orthorhombic, P2 ₁ 2 ₁ 2 ₁	triclinic, P $\bar{1}$
unit cell dimensions			
<i>a</i> , <i>b</i> , <i>c</i> , Å	24.630(8), 9.2476(21), 18.735(4)	12.590(3), 18.188(3), 20.804(5)	12.7329(19), 13.450(4), 13.7936(20)
α , β , γ , deg	90, 101.710(20), 90	90, 90, 90	76.770(16), 73.305(14), 76.017(16)
volume Å ³	4178.4(18)	4764.1(17)	2163.1(7)
<i>Z</i>	4	4	2
Formula weight	958.75	1080.99	1064.8
<i>D</i> _{calc} , g/cm ³	1.524	1.507	1.635
no. of orientatn rflns	24	26	24
2 θ range, deg	18.32–24.52	18.74–23.42	18.70–22.56
<i>h</i> , <i>k</i> , <i>l</i> ranges	–29 to 28, 0 to 10, 0 to 22	0 to 14, 0 to 21, 0 to 24	–14 to 15, 0 to 15, –15 to 16
abs cor		Ψ scan	
abs coeff, mm ⁻¹	1.60	0.73	0.83
transm range	0.9515–0.9947	0.9503–0.9993	0.9377–0.9993
F(000)	2319.78	1928	1060
diffractometer used		Nonius CAD4	
radiation; λ , Å		Mo K α ; 0.70930	
temperature (K)		297	
scan type		$\theta/2\theta$	
2 θ range, deg		2–50	
scan speed, deg/min	16.48/2–16.48/7	16.48/2–16.48/9	16.48/2–16.48/10
std rflns		3 std/7200 sec	
decay, %	≤ 1	≤ 2	≤ 2
no. of unique rflns	3669	4635	7583
no. of rflns (<i>N</i> _o) used	3243 with <i>I</i> > 2.0 σ (<i>I</i>)	3410 with <i>I</i> > 2.0 σ (<i>I</i>)	5543 with <i>I</i> > 2.0 σ (<i>I</i>)
no. of atoms refined	47	106	94
no. of params (<i>N</i> _v) refined	254	596	538
max Δ/σ ratio	0.061	0.181	0.280
<i>R</i> , <i>R</i> _w , <i>S</i> ^a	0.0264, 0.025, 2.74	0.033, 0.026, 1.43	0.054, 0.047, 3.16
resid peak; hole, e/Å ³	0.30, –0.46	1.46, –1.78 ^b	1.78, –1.16 ^b

^a $S = [\sum \omega |F_o - F_c|^2 / (N_o - N_v)]^{1/2}$, $\omega^{-1} = \sigma^2(F_o)$; ^b Ghost peaks.

TABLE 2. Fractional atomic coordinates and B_{iso} ^a for 1–3

	<i>x</i>	<i>y</i>	<i>z</i>	B_{iso}
(a) Compound 1				
Ru	0.449381(9)	0.44438(3)	0.203545(13)	2.135(10)
P	0.36479(3)	0.37055(9)	0.11831(4)	2.24(3)
O1	0.48535(8)	0.27780(23)	0.15177(11)	3.28(10)
O2	0.43112(8)	0.28018(24)	0.27477(11)	3.54(11)
C1	0.53247(12)	0.2284(3)	0.17213(16)	2.84(14)
C2	0.54932(15)	0.1019(4)	0.13206(21)	5.46(20)
C3	0.47073(12)	0.5828(4)	0.14496(17)	3.20(14)
O3	0.48409(10)	0.6706(3)	0.10862(14)	5.60(13)
C4	0.42082(11)	0.5893(3)	0.25191(17)	3.05(14)
O4	0.40372(9)	0.6825(3)	0.28150(13)	4.74(12)
C11	0.35293(12)	0.4635(3)	0.03085(15)	2.55(13)
C12	0.39717(13)	0.4707(4)	−0.00579(17)	3.49(16)
C13	0.39118(15)	0.5374(4)	−0.07253(18)	4.45(19)
C14	0.34110(16)	0.5985(4)	−0.10433(19)	5.01(20)
C15	0.29672(15)	0.5914(4)	−0.06943(19)	4.65(18)
C16	0.30222(12)	0.5236(3)	−0.00241(17)	3.33(15)
C21	0.29904(11)	0.3906(3)	0.14807(15)	2.41(13)
C22	0.28686(13)	0.5214(4)	0.17752(19)	4.23(17)
C23	0.23688(14)	0.5381(5)	0.20114(19)	5.36(20)
C24	0.19993(13)	0.4238(5)	0.19531(19)	5.10(21)
C25	0.21160(13)	0.2973(4)	0.16518(20)	4.53(18)
C26	0.26063(12)	0.2793(4)	0.14163(17)	3.37(15)
C31	0.36480(11)	0.1804(3)	0.09240(15)	2.43(13)
C32	0.35247(14)	0.1345(4)	0.02114(17)	3.60(16)
C33	0.35229(15)	−0.0116(4)	0.00412(19)	4.43(18)
C34	0.36608(15)	−0.1119(4)	0.05822(21)	4.73(19)
C35	0.37800(16)	−0.0677(4)	0.12935(20)	5.10(20)
C36	0.37776(14)	0.0771(4)	0.14697(17)	3.93(17)
(b) Compound 2				
Ru1	0.37036(4)	0.50346(4)	0.050587(24)	2.212(21)
Ru2	0.53481(4)	0.49549(4)	−0.035473(24)	2.170(21)
P1	0.25134(15)	0.51109(13)	0.14271(8)	2.42(8)
P2	0.70566(15)	0.48653(12)	−0.08990(9)	2.45(8)
O1	0.4633(4)	0.5873(3)	0.09294(23)	3.21(25)
O2	0.5937(4)	0.5798(3)	0.02256(23)	3.14(24)
O3	0.4649(4)	0.4279(3)	0.10344(22)	3.15(25)
O4	0.6025(4)	0.4228(3)	0.03414(23)	3.3(3)
O5	0.2504(5)	0.3848(3)	−0.0161(3)	5.3(3)
O6	0.2354(5)	0.6064(4)	−0.0250(3)	6.1(4)
O7	0.4362(5)	0.6051(3)	−0.1243(3)	5.1(3)
O8	0.4407(5)	0.3781(3)	−0.1173(3)	5.8(4)
C1	0.5532(6)	0.6066(4)	0.0715(3)	2.6(3)
C11	0.6112(6)	0.6654(4)	0.1077(3)	3.0(4)
C12	0.5829(7)	0.6837(5)	0.1690(4)	4.8(5)
C13	0.6394(8)	0.7359(5)	0.2031(5)	6.1(6)
C14	0.7236(8)	0.7678(5)	0.1743(5)	6.7(6)
C15	0.7570(7)	0.7509(5)	0.1135(5)	5.2(5)
C16	0.6990(6)	0.6981(4)	0.0797(4)	3.6(4)
C2	0.5549(6)	0.4040(4)	0.0853(3)	2.4(3)
C21	0.6079(6)	0.3479(4)	0.1261(4)	2.8(3)
C22	0.5731(7)	0.3360(5)	0.1882(4)	4.2(4)
C23	0.6207(8)	0.2816(5)	0.2252(4)	5.4(5)
C24	0.6969(8)	0.2376(5)	0.1994(4)	5.6(5)
C25	0.7310(7)	0.2481(5)	0.1379(4)	4.5(5)
C26	0.6864(7)	0.3043(4)	0.1016(4)	3.5(4)
C5	0.2953(6)	0.4295(4)	0.0096(4)	3.1(4)
C6	0.2922(7)	0.5686(4)	0.0041(4)	3.5(4)
C7	0.4749(7)	0.5628(4)	−0.0903(4)	3.3(4)
C8	0.4764(7)	0.4228(4)	−0.0851(4)	3.5(4)
C11A	0.1548(6)	0.4364(4)	0.1410(3)	2.6(3)

TABLE 2 (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	B_{iso}
C12A	0.1621(8)	0.3774(5)	0.1799(4)	5.3(5)
C13A	0.0902(10)	0.3190(5)	0.1729(6)	8.1(7)
C14A	0.0147(8)	0.3199(5)	0.1269(5)	6.8(6)
C15A	0.0069(8)	0.3790(6)	0.0879(5)	6.3(6)
C16A	0.0751(7)	0.4389(5)	0.0939(4)	4.3(4)
C11B	0.3073(5)	0.5065(6)	0.2239(3)	3.3(4)
C12B	0.2433(6)	0.5070(9)	0.2772(3)	5.4(5)
C13B	0.2846(6)	0.5041(10)	0.3377(3)	6.6(6)
C14B	0.3907(6)	0.5000(9)	0.3459(3)	7.1(6)
C15B	0.4562(6)	0.5027(10)	0.2945(3)	7.5(6)
C16B	0.4151(6)	0.5070(8)	0.2324(3)	5.5(5)
C11C	0.1718(6)	0.5954(4)	0.1490(3)	2.6(3)
C12C	0.0725(7)	0.5962(4)	0.1770(4)	3.5(4)
C13C	0.0197(7)	0.6634(5)	0.1833(4)	5.1(5)
C14C	0.0670(8)	0.7271(5)	0.1631(4)	5.3(5)
C15C	0.1649(8)	0.7270(4)	0.1350(5)	5.1(5)
C16C	0.2179(7)	0.6614(4)	0.1291(4)	3.8(4)
C21A	0.7734(6)	0.3988(4)	−0.0822(4)	3.1(4)
C22A	0.8811(8)	0.3940(5)	−0.0858(5)	5.7(5)
C23A	0.9326(8)	0.3252(6)	−0.0836(5)	6.9(6)
C24A	0.8759(9)	0.2631(5)	−0.0759(5)	6.4(6)
C25A	0.7688(8)	0.2669(5)	−0.0734(4)	5.1(5)
C26A	0.7187(7)	0.3342(5)	−0.0758(4)	4.2(4)
C21B	0.6996(5)	0.4994(6)	−0.1770(3)	2.9(3)
C22B	0.6624(7)	0.5667(4)	−0.2000(4)	3.7(4)
C23B	0.6575(7)	0.5795(5)	−0.2653(4)	4.7(5)
C24B	0.6886(7)	0.5263(5)	−0.3075(4)	5.0(5)
C25B	0.7266(8)	0.4600(5)	−0.2864(4)	5.8(6)
C26B	0.7315(7)	0.4468(5)	−0.2202(4)	4.1(4)
C21C	0.8055(6)	0.5508(4)	−0.0613(3)	2.7(3)
C22C	0.8303(7)	0.5474(5)	0.0023(4)	4.4(5)
C23C	0.9085(8)	0.5927(6)	0.0272(4)	6.2(6)
C24C	0.9616(8)	0.6414(6)	−0.0103(5)	6.9(6)
C25C	0.9362(8)	0.6466(6)	−0.0720(5)	6.6(6)
C26C	0.8616(8)	0.6020(5)	−0.0981(4)	5.2(5)
(c) Compound 3				
Ru1	0.38673(5)	0.27446(5)	0.23389(5)	2.57(3)
Ru2	0.29736(5)	0.16748(5)	0.14176(5)	2.53(3)
P1	0.42980(17)	0.37113(15)	0.34295(15)	2.74(10)
P2	0.17462(16)	0.09318(15)	0.08186(16)	2.69(9)
O1	0.2423(4)	0.3901(4)	0.2154(4)	3.9(3)
O2	0.1984(4)	0.3189(4)	0.1026(4)	3.3(3)
O3	0.2765(4)	0.2095(4)	0.3712(4)	3.6(3)
O4	0.1769(4)	0.1587(4)	0.2873(4)	3.5(3)
C1	0.1891(6)	0.3876(5)	0.1534(6)	3.1(4)
C2	0.0935(8)	0.4855(7)	0.1453(9)	7.5(8)
F1 ^b	0.1356(7)	0.5597(6)	0.0778(6)	8.46(23)
F2 ^b	0.0682(7)	0.5387(6)	0.2141(6)	7.78(21)
F3 ^b	−0.0017(7)	0.4602(7)	0.1729(7)	9.3(3)
F4 ^b	0.0584(8)	0.4861(7)	0.0615(7)	10.9(3)
C3	0.1974(7)	0.1769(6)	0.3634(6)	3.5(4)
C4	0.1032(10)	0.1576(10)	0.4671(8)	8.6(8)
F5 ^b	0.1579(9)	0.0977(8)	0.5353(8)	12.3(3)
F6 ^b	0.0869(7)	0.2219(7)	0.5229(7)	8.82(24)
F7 ^b	0.0074(8)	0.1734(7)	0.4530(7)	9.7(3)
F8 ^b	0.0916(9)	0.0596(8)	0.4792(8)	11.6(3)
C5	0.5075(6)	0.1691(6)	0.2409(6)	3.4(4)
O5	0.5829(5)	0.1028(4)	0.2437(5)	5.3(4)
C6	0.4657(7)	0.3362(6)	0.1108(6)	3.6(4)
O6	0.5117(5)	0.3760(5)	0.0335(4)	5.7(4)
C7	0.4101(7)	0.1769(6)	0.0227(6)	3.5(4)

TABLE 2 (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso}
O7	0.4844(5)	0.1763(5)	-0.0460(4)	5.6(4)
C8	0.3832(6)	0.0431(6)	0.1831(6)	3.2(4)
O8	0.4376(5)	-0.0339(4)	0.2088(5)	4.9(3)
C11A	0.5145(6)	0.2882(6)	0.4287(5)	2.9(4)
C12A	0.6011(7)	0.3199(6)	0.4469(6)	3.8(4)
C13A	0.6669(7)	0.2539(8)	0.5087(7)	5.2(6)
C14A	0.6444(8)	0.1565(8)	0.5530(7)	5.7(6)
C15A	0.5566(8)	0.1238(6)	0.5372(7)	5.0(5)
C16A	0.4914(7)	0.1903(6)	0.4751(6)	3.9(5)
C11B	0.5146(6)	0.4699(6)	0.2757(6)	2.9(4)
C12B	0.4865(7)	0.5707(6)	0.2942(6)	4.0(5)
C13B	0.5578(8)	0.6407(7)	0.2420(7)	5.4(6)
C14B	0.6548(8)	0.6101(7)	0.1743(7)	5.8(6)
C15B	0.6833(7)	0.5107(8)	0.1536(7)	5.3(5)
C16B	0.6136(7)	0.4401(6)	0.2036(6)	4.1(4)
C11C	0.3111(6)	0.4397(5)	0.4274(6)	3.0(4)
C12C	0.2275(7)	0.5071(6)	0.3871(6)	4.2(5)
C13C	0.1376(7)	0.5604(7)	0.4492(7)	5.1(5)
C14C	0.1274(8)	0.5477(7)	0.5513(7)	5.6(5)
C15C	0.2080(8)	0.4802(7)	0.5941(7)	5.4(6)
C16C	0.3004(7)	0.4270(6)	0.5328(6)	4.1(4)
C21A	0.1758(6)	0.1384(5)	-0.0532(6)	3.0(4)
C22A	0.2772(7)	0.1210(6)	-0.1255(6)	3.6(4)
C23A	0.2836(8)	0.1560(7)	-0.2288(6)	5.0(5)
C24A	0.1883(9)	0.2086(7)	-0.2604(7)	5.7(6)
C25A	0.0890(9)	0.2258(7)	-0.1899(7)	6.0(6)
C26A	0.0815(7)	0.1905(6)	-0.0867(6)	4.0(5)
C21B	0.0282(6)	0.1193(6)	0.1506(6)	3.0(4)
C22B	-0.0363(7)	0.0430(6)	0.1867(7)	4.2(5)
C23B	-0.1451(7)	0.0658(7)	0.2409(7)	5.1(5)
C24B	-0.1919(7)	0.1627(8)	0.2641(7)	5.3(5)
C25B	-0.1295(7)	0.2395(7)	0.2274(9)	6.7(7)
C26B	-0.0194(7)	0.2180(7)	0.1721(8)	5.5(6)
C21C	0.2070(6)	-0.0487(5)	0.0972(6)	3.0(4)
C22C	0.2173(7)	-0.1043(6)	0.1930(7)	4.4(5)
C23C	0.2405(8)	-0.2119(7)	0.2092(7)	5.4(6)
C24C	0.2549(8)	-0.2636(7)	0.1319(8)	5.9(6)
C25C	0.2440(8)	-0.2110(7)	0.0360(7)	5.2(5)
C26C	0.2192(7)	-0.1021(6)	0.0192(6)	4.0(4)

^a *B*_{iso} is the mean of the principal axes of the thermal ellipsoid;

^b occupancy = 0.75.

lengths, we compare Mo–O (equatorial, bridging carboxylates), Mo–CO (equatorial carbonyl) and Mo–L (axial ligands) distances from all the reported structures of $[Ru_2(O_2CR)_2(CO)_4L_2]$ (L = CO, PPh₃, PBu₃, py, H₂O, or PhCO₂H; R = Me, CF₃, ⁿPr, or 4-FC₆H₄) and $[Ru_2(O_2CPh)_2(CO)_4]_n$ [10,11,15,16] in Table 4. From this table, the mild inductive effect of R is reflected in the bond lengths of 2.736 Å for **1** (R = Me, L = PPh₃); 2.741 Å for **2** (R = Ph, L = PPh₃) and 2.728 Å for **3** (R = CF₃, L = PPh₃) but a rather strong axial coordination effect is shown in terms of R, L, and d(Ru–Ru): Me, CO, 2.689; Me, py, 2.678; Me, PPh₃, 2.736; Ph, CO, 2.704; Ph, PhCO₂H, 2.637; Ph, PPh₃, 2.741 Å. The differing sensitivities of Ru–Ru lengths to axial coordination and inductive effect can be ratio-

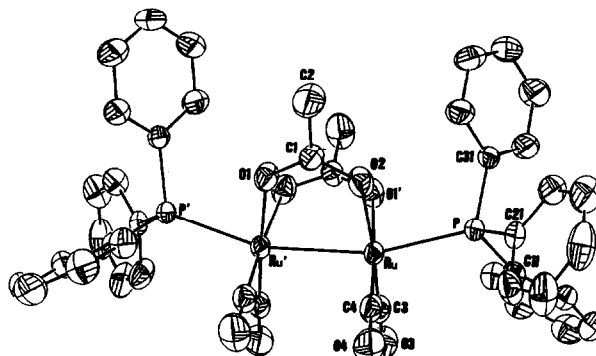


Fig. 1. ORTEP drawing of $[Ru_2(O_2CMe)_2(CO)_4(PPh_3)_2]$ (**1**) with the numbering scheme. A C₂ axis is imposed crystallographically at the centre of the Ru–Ru bond. Thermal ellipsoids are drawn at the 50% probability level.

nalized by applying the molecular-orbital calculation results for HVCs [12c,g, 21–24] and the formal electron configuration of $\sigma^2\pi^4\delta^2\delta^*\pi^{*4}$ in the Ru₂ compounds in Table 4. When π -acids such as CO coordinate axially with the Ru₂ dimer, electron-drainage from the filled M–M antibonding orbitals (δ^* or π^*) to the CO π^* orbitals strengthens the M–M bonding interaction by increasing the M–M bond order. However, when the axial ligands are strong σ -donors with or without some weak π -accepting ability such as py or PPh₃, the M–M bond order decreases by bonding interactions through the empty M–M antibonding orbitals (σ^*). Following the results of calculation, it is obvious that the through-bond coupling [21,25], which is negative for **1**, **2**, or **3**, is determined primarily by the relative disposition of the bridging carboxylates with respect to the metal centers (*i.e.*, the Ru–O distances). As evidenced in the averaged Ru–O and Ru–Ru dis-

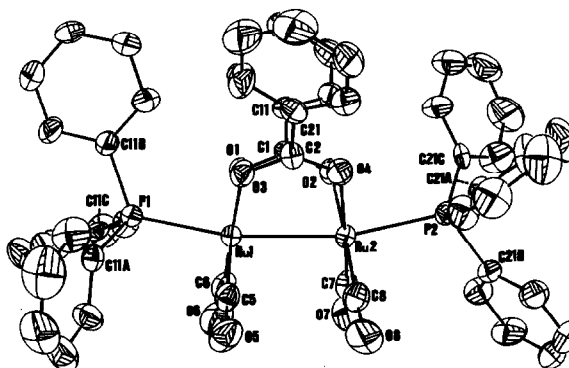


Fig. 2. ORTEP drawing of $[Ru_2(O_2CPh)_2(CO)_4(PPh_3)_2]$ (**2**) with the numbering scheme. One disordered CF₃ group presented by one carbon atom and four fluorine atoms with occupancy = 0.75 is drawn whereas the other disordered CF₃ group is not drawn for clarity. Atom C(5) hides behind atoms C(6) and O(6). Thermal ellipsoids are drawn at the 50% probability level.

TABLE 3. Selected bond lengths and angles for 1–3

<i>(a) Compound 1</i>			
Ru–Ru'	2.7360(9)	P–C(21)	1.826(3)
Ru–P	2.4508(10)	P–C(31)	1.825(3)
Ru–O(1)	2.1089(20)	O(1)–C(1)	1.233(3)
Ru–O(2)	2.1289(21)	O(2)–C(1)	1.289(4)
Ru–C(3)	1.831(3)	C(1)–C(2)	1.494(5)
Ru–C(4)	1.836(3)	C(3)–O(3)	1.150(4)
P–C(11)	1.821(3)	C(4)–O(4)	1.150(4)
Ru'–Ru–P	163.539(23)	C(3)–Ru–C(4)	88.34(14)
Ru'–Ru–O(1)'	83.05(5)	Ru–P–C(11)	114.50(10)
Ru'–Ru–O(2)	83.25(6)	Ru–P–C(21)	117.52(10)
Ru'–Ru–C(3)	92.63(9)	Ru–P–C(31)	113.32(9)
Ru'–Ru–C(4)	94.41(9)	C(11)–P–C(21)	103.68(13)
P–Ru–O(1)	82.98(6)	C(11)–P–C(31)	102.97(13)
P–Ru–O(2)	87.13(6)	C(21)–P–C(31)	103.13(13)
P–Ru–C(3)	96.53(9)	Ru–O(1)'–C(1)'	125.80(19)
P–Ru–C(4)	99.48(9)	Ru–O(2)–C(1)	123.12(18)
O(1)'–Ru–O(2)	85.94(9)	O(1)–C(1)–O(2)	124.4(3)
O(1)'–Ru–C(3)	92.09(12)	O(1)–C(1)–C(2)	118.3(3)
O(1)'–Ru–C(4)	177.44(10)	O(2)–C(1)–C(2)	117.3(3)
O(2)–Ru–C(3)	175.61(10)	Ru–C(3)–O(3)	179.4(3)
O(2)–Ru–C(4)	93.46(12)	Ru–C(4)–O(4)	178.3(3)
<i>(b) Compound 2</i>			
Ru(1)–Ru(2)	2.7411(8)	P(2)–C(21A)	1.817(8)
Ru(1)–P(1)	2.4367(19)	P(2)–C(21B)	1.828(6)
Ru(1)–O(1)	2.114(5)	P(2)–C(21C)	1.816(7)
Ru(1)–O(3)	2.124(5)	O(1)–C(1)	1.266(9)
Ru(1)–C(5)	1.851(8)	O(2)–C(1)	1.239(9)
Ru(1)–C(6)	1.819(8)	O(3)–C(2)	1.271(9)
Ru(2)–P(2)	2.4364(20)	O(4)–C(2)	1.269(8)
Ru(2)–O(2)	2.088(5)	O(5)–C(5)	1.127(9)
Ru(2)–O(4)	2.138(5)	O(6)–C(6)	1.162(10)
Ru(2)–C(7)	1.835(8)	O(7)–C(7)	1.154(9)
Ru(2)–C(8)	1.830(8)	O(8)–C(8)	1.146(9)
Ru(2)–C(8)	1.830(8)	O(8)–C(8)	1.146(9)
P(1)–C(11A)	1.824(7)	C(1)–C(11)	1.497(10)
P(1)–C(11B)	1.832(6)	C(2)–C(21)	1.486(10)
P(1)–C(11C)	1.835(7)		
Ru(2)–Ru(1)–P(1)	168.89(5)	C(5)–Ru(1)–C(6)	87.2(4)
Ru(2)–Ru(1)–O(1)	83.83(13)	Ru(1)–Ru(2)–P(2)	166.91(5)
Ru(2)–Ru(1)–O(3)	83.14(13)	Ru(1)–Ru(2)–O(2)	81.46(13)
Ru(2)–Ru(1)–C(5)	92.67(24)	Ru(1)–Ru(2)–O(4)	83.75(14)
Ru(2)–Ru(1)–C(6)	95.50(25)	Ru(1)–Ru(2)–C(7)	93.45(24)
P(1)–Ru(1)–O(1)	88.36(14)	Ru(1)–Ru(2)–C(8)	95.9(3)
P(1)–Ru(1)–O(3)	88.53(14)	P(2)–Ru(2)–O(2)	90.26(14)
P(1)–Ru(1)–C(5)	95.13(24)	P(2)–Ru(2)–O(4)	85.51(14)
P(1)–Ru(1)–C(6)	92.78(25)	P(2)–Ru(2)–C(7)	96.81(25)
O(1)–Ru(1)–O(3)	86.59(20)	P(2)–Ru(2)–C(8)	92.5(3)
O(1)–Ru(1)–C(5)	176.5(3)	O(2)–Ru(2)–O(4)	85.48(20)
O(1)–Ru(1)–C(6)	93.0(3)	O(2)–Ru(2)–C(7)	90.9(3)
O(3)–Ru(1)–C(5)	93.1(3)	O(2)–Ru(2)–C(8)	177.1(3)
O(3)–Ru(1)–C(6)	178.6(3)	O(4)–Ru(2)–C(7)	175.7(3)
Ru(1)–C(5)–O(5)	179.0(7)	O(4)–Ru(2)–C(8)	95.5(3)
Ru(1)–C(6)–O(6)	174.6(8)	C(7)–Ru(2)–C(8)	88.1(3)
Ru(2)–C(7)–O(7)	179.2(7)	O(1)–C(1)–O(2)	123.2(7)
Ru(2)–C(8)–O(8)	178.5(7)	O(1)–C(1)–C(11)	117.2(6)
Ru(1)–O(1)–C(1)	123.3(4)	O(2)–C(1)–C(11)	119.6(7)
Ru(2)–O(2)–C(1)	128.2(5)	O(3)–C(2)–O(4)	125.3(6)
Ru(1)–O(3)–C(2)	124.6(4)	O(3)–C(2)–C(21)	117.8(6)
Ru(2)–O(4)–C(2)	123.2(5)	O(4)–C(2)–C(21)	116.9(6)

TABLE 3 (continued)

(c) Compound 3			
Ru(1)–Ru(2)	2.7276(9)	P(1)–C(11A)	1.832(8)
Ru(1)–P(1)	2.4430(21)	P(1)–C(11B)	1.828(7)
Ru(1)–O(1)	2.138(5)	P(1)–C(11C)	1.816(7)
Ru(1)–O(3)	2.151(5)	P(2)–C(21A)	1.820(8)
Ru(1)–C(5)	1.831(8)	P(2)–C(21B)	1.821(7)
Ru(1)–C(6)	1.833(8)	P(2)–C(21C)	1.828(7)
Ru(2)–P(2)	2.4492(21)	O(1)–C(1)	1.245(9)
Ru(2)–O(2)	2.162(5)	O(2)–C(1)	1.248(9)
Ru(2)–O(4)	2.146(5)	O(3)–C(3)	1.231(9)
Ru(2)–C(7)	1.847(8)	O(4)–C(3)	1.239(9)
Ru(2)–C(8)	1.832(8)	C(1)–C(2)	1.569(11)
		C(3)–C(4)	1.596(13)
		C(1)–C(2)	1.569(11)
		C(3)–C(4)	1.596(13)
		C(5)–O(5)	1.144(9)
		C(6)–O(6)	1.139(10)
		C(7)–O(7)	1.131(9)
		C(8)–O(8)	1.142(9)
Ru(2)–Ru(1)–P(1)	168.11(6)	O(3)–Ru(1)–C(6)	173.1(3)
Ru(2)–Ru(1)–O(1)	82.36(13)	C(5)–Ru(1)–C(6)	89.7(4)
Ru(2)–Ru(1)–O(3)	83.15(13)	Ru(1)–Ru(2)–P(2)	166.22(5)
Ru(2)–Ru(1)–C(5)	92.21(23)	Ru(1)–Ru(2)–O(2)	83.08(13)
Ru(2)–Ru(1)–C(6)	92.92(24)	Ru(1)–Ru(2)–O(4)	82.20(13)
P(1)–Ru(1)–O(1)	91.27(14)	Ru(1)–Ru(2)–C(7)	92.90(23)
P(1)–Ru(1)–O(3)	86.28(14)	Ru(1)–Ru(2)–C(8)	92.69(23)
P(1)–Ru(1)–C(5)	94.32(23)	P(2)–Ru(2)–O(2)	87.88(14)
P(1)–Ru(1)–C(6)	97.04(24)	P(2)–Ru(2)–O(4)	86.77(14)
O(1)–Ru(1)–O(3)	84.67(21)	P(2)–Ru(2)–C(7)	98.37(24)
O(1)–Ru(1)–C(5)	174.4(3)	P(2)–Ru(2)–C(8)	95.98(23)
O(1)–Ru(1)–C(6)	89.2(3)		
O(3)–Ru(1)–C(5)	96.1(3)		
Ru(1)–O(1)–C(1)	121.0(4)	O(2)–Ru(2)–O(4)	85.67(19)
Ru(2)–O(2)–C(1)	118.6(5)	O(2)–Ru(2)–C(7)	95.8(3)
Ru(1)–O(3)–C(3)	118.9(5)	O(2)–Ru(2)–C(8)	175.5(3)
Ru(2)–O(4)–C(3)	120.6(5)	O(4)–Ru(2)–C(7)	174.7(3)
O(1)–C(1)–O(2)	129.8(7)	O(4)–Ru(2)–C(8)	92.2(3)
O(1)–C(1)–C(2)	112.1(7)	C(7)–Ru(2)–C(8)	85.9(3)
O(2)–C(1)–C(2)	118.0(7)		
Ru(1)–C(5)–O(5)	178.8(7)		
Ru(1)–C(6)–O(6)	177.9(7)		
Ru(2)–C(7)–O(7)	174.3(7)		
Ru(2)–C(8)–O(8)	179.3(7)		

TABLE 4. Structures of [Ru₂(O₂CR)₂(CO)₄L₂]

Compound		Averaged interatomic distances, Å				
R	2 L	Ru–O	Ru–CO	Ru–L	Ru–Ru	Reference
Me	2 CO	2.094	1.845	1.976	2.689	11
Me	2 py	– ^a	1.84	– ^a	2.678	10
Me	2 PPh ₃	2.119	1.834	2.451	2.736	This work
CF ₃	2 PPh ₃	2.149	1.836	2.446	2.728	This work
Pr ⁿ	2 P ^t Bu ₃	2.13	1.83	2.622	2.728	15
4-F-C ₄ H ₄	(CO, H ₂ O)	2.119	1.851	1.999 ^b , 2.999 ^c	2.649	16
Ph	2 PhCO ₂ H ^d	2.134	1.834	2.265	2.637	16
Ph	2 PhCO ₂ ^e	2.130	1.829	2.299	2.639	11
Ph	2 CO	2.108	1.840	2.013	2.704	11
Ph	2 PPh ₃	2.116	1.834	2.437	2.741	This work

^a Only the Ru–Ru and Ru–CO distances were cited previously [10]; ^b Ru–CO distance; ^c Ru–OH₂ distance; ^d There exist two intramolecular hydrogen bonds between PhCO₂H and one bridging PhCOO ligand; ^e Oxygen atoms of the neighboring bridging carboxylates coordinate with the Ru atoms in axial positions.

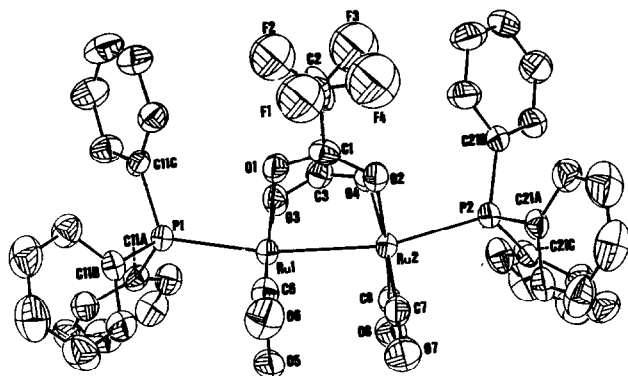


Fig. 3. ORTEP drawing of $[Ru_2(O_2CCF_3)_2(CO)_4(PPh_3)_2]$ (**3**) with the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

tances of 2.116, 2.741 Å in **2**; 2.119, 2.736 Å in **1**; and 2.149, 2.728 Å in **3**, respectively, it is apparent that the longer the Ru–O distance, the weaker the negative coupling (and the shorter the Ru–Ru distance). Thus, the observed mild inductive effect is probably due to the small range of 0.033 Å in the Ru–O distances, if a dinuclear compound, $[Ru_2(O_2CR)_2(CO)_4(PPh_3)_2]$, can be prepared with rather long Ru–O distances, the Ru–Ru distance in this compound should be quite short and an appreciable inductive effect should be observed.

The Ru–P lengths of 2.4508(10) Å in **1**, 2.4367(19), 2.4364(20) Å in **2**, and 2.4430(21), 2.4492(21) Å in **3**, are similar to each other and typical of the Ru–P distances found in other mononuclear [26] or dinuclear [15] ruthenium complexes containing two phosphine groups, although the Ru–Ru–P angle of 163.539(23)° in **1** is much smaller than those of 168.89(5), 166.91(5)° in **2** and 168.11(6), 166.22(5)° in **3**. As reflected in the similar $^{31}P\{^1H\}$ NMR chemical shift around 20 ppm observed for PPh_3 in **1–3**, the bonding interactions between the Ru^I atoms and the phosphines of these compounds in solution should be very close to each other [27].

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