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# Structural characterization and comparison of $[Ru_2(O_2CR)_2(CO)_4L_2]$

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## Abstract

The structures of $[Ru_2(CO)_4(O_2CR)_2(PPh_3)_2]$ (R = 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, $\beta = 101.710(20)°$, $Z = 4$, $R = 0.026$, $R_w = 0.025$, 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, $a = 76.770(16)$, $\beta = 73.305(14)$, $\gamma = 76.017(16)°$, $Z = 2$, $R = 0.054$, $R_w = 0.047$, 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 $[Ru_2(O_2CR)_2(CO)_4L_2]$ (L = CO. $PPh_3$, $PBu_3$, py, $H_2O$, or $PhCO_2H$; R = Me, $CF_3$, $^nPr$, or $4\text{-}FC_6H_4$) or of $[Ru_2(O_2CPh)_2(CO)_4]_\infty$ 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 $[Ru_2(O_2CR)_2(CO)_4L_2]$ 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 $[Ru_3(CO)_{12}]$ [3] and the well-established, multiply bonded dimers such as $[Ru_2(O_2CR)_4Cl]$ [4]. In this paper, we present the structural details of $[Ru_2(O_2CR)_2(CO)_4(PPh_3)_2]$ R = 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 $[M_2(O_2CR)_4L_2]$ (M = Mo, Cr, or Rh) [12] have been reported in the literature. We hope that the comparison in $[Ru_2(O_2CR)_2(CO)_4L_2]$ 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, $[Ru_2(O_2CR)_2(CO)_4(PPh_3)_2]$ (R = Me, **1**; Ph, **2**; or $CF_3$, **3**), were prepared by the published procedure [9,13]. $^{31}P\{^1H\}$ 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 $CF_3$ 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 structure, 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, $[Ru_2(O_2CR)_2(CO)_4L_2]$ with L = py, CO, $P^tBu_3$, $H_2O$, or $PhCO_2H$ and R = Me, $^n$Pr, 4-F-$C_6H_4$ or Ph [10,11,15,16] and $[Ru_2X_2(CO)_4(PR_3)_2]$ with $X^-$ = $Cl^-$, 3,5-dimethylpyrazolato ($Pz'^-$), or 2-oxypyridinato ($NC_5H_4O^-$); R = Ph, $^t$Bu, or *p*-tol [17–19] but different from the *cis*-staggered structure observed for the unbridged dinuclear compound, $[Ru_2(HBPz_3)_2(CO)_4]$ (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, $[Ru_2(HBPz_3)_2(CO)_4]$ [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 | $C_{44}H_{38}O_8P_2Ru_2$ | $C_{54}H_{40}O_8P_2Ru_2$ | $C_{44}H_{30}F_6O_8P_2Ru_2$ |
| 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, $P2_12_12_1$ | triclinic, $P\bar{1}$ |
| unit cell dimensions | | | |
| $a, b, c$, 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) |
| $\alpha, \beta, \gamma$, 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) |
| $Z$ | 4 | 4 | 2 |
| Formula weight | 958.75 | 1080.99 | 1064.8 |
| $D_{calc}$, g/cm$^3$ | 1.524 | 1.507 | 1.635 |
| no. of orientatn rflns | 24 | 26 | 24 |
| $2\theta$ range, deg | 18.32–24.52 | 18.74–23.42 | 18.70–22.56 |
| $h, k, l$ 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 | | $\Psi$ 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; $\lambda$, Å | | Mo K$\alpha$; 0.70930 | |
| temperature (K) | | 297 | |
| scan type | | $\theta/2\theta$ | |
| $2\theta$ 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 ($N_o$) used | 3243 with $I > 2.0\sigma(I)$ | 3410 with $I > 2.0\sigma(I)$ | 5543 with $I > 2.0\sigma(I)$ |
| no. of atoms refined | 47 | 106 | 94 |
| no. of params ($N_v$) refined | 254 | 596 | 538 |
| max $\Delta/\sigma$ ratio | 0.061 | 0.181 | 0.280 |
| $R$, $R_\omega$ S [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] $S = [\Sigma\omega|F_o - F_c|^2/(N_o - N_v)]^{1/2}$, $\omega^{-1} = \sigma^2(F_o)$; [b] Ghost peaks.

TABLE 2. Fractional atomic coordinates and $B_{\mathrm{iso}}$ [a] for **1**–**3**

| | $x$ | $y$ | $z$ | $B_{\mathrm{iso}}$ |
|---|---|---|---|---|
| (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) |
| 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)

| | $x$ | $y$ | $z$ | $B_{iso}$ |
|---|---|---|---|---|
| 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.

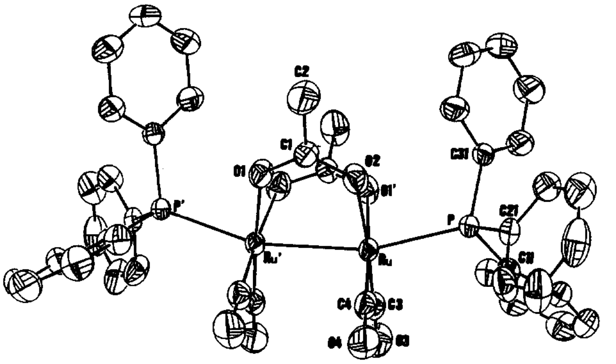

Fig. 1. ORTEP drawing of [$Ru_2(O_2CMe)_2(CO)_4(PPh_3)_2$] (**1**) with the numbering scheme. A $C_2$ axis is imposed crystallographically at the centre of the Ru–Ru bond. Thermal ellipsoids are drawn at the 50% probability level.

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. $PPh_3$, $PBu_3$, py, $H_2O$, or $PhCO_2H$; R = Me, $CF_3$, $^nPr$, or 4-$FC_6H_4$) and [$Ru_2(O_2CPh)_2(CO)_4$]$_\infty$ [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 = $PPh_3$); 2.741 Å for **2** (R = Ph, L = $PPh_3$) and 2.728 Å for **3** (R = $CF_3$, L = $PPh_3$) 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, $PPh_3$, 2.736; Ph, CO, 2.704; Ph, $PhCO_2H$, 2.637; Ph, $PPh_3$, 2.741 Å. The differing sensitivities of Ru–Ru lengths to axial coordination and inductive effect can be rationalized by applying the molecular-orbital calculation results for HVCs [12c,g, 21–24] and the formal electron configuration of $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ in the $Ru_2$ compounds in Table 4. When $\pi$-acids such as CO coordinate axially with the $Ru_2$ dimer, electron-drainage from the filled M–M antibonding orbitals ($\delta^*$ or $\pi^*$) to the CO $\pi^*$ orbitals strengthens the M–M bonding interaction by increasing the M–M bond order. However, when the axial ligands are strong $\sigma$-donors with or without some weak $\pi$-accepting ability such as py or $PPh_3$, the M–M bond order decreases by bonding interactions through the empty M–M antibonding orbitals ($\sigma^*$). 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-

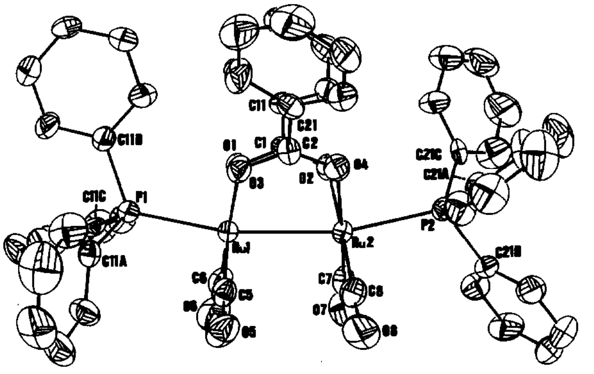

Fig. 2. ORTEP drawing of [$Ru_2(O_2CPh)_2(CO)_4(PPh_3)_2$] (**2**) with the numbering scheme. One disordered $CF_3$ group presented by one carbon atom and four fluorine atoms with occupancy = 0.75 is drawn whereas the other disordered $CF_3$ group is not drawn for clarity. Atom C(5) hides behind atoms C(6) and O(6). Thermal ellipsoids are drawn at the 50% probability level.

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

| | | | |
|---|---|---|---|
| *(a) Compound 1* | | | |
| 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) |
| *(b) Compound 2* | | | |
| 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) |
| Ru(2)–C(8) | 1.832(8) | 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 $[Ru_2(O_2CR)_2(CO)_4L_2]$

| 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 $P^tBu_3$ | 2.13 | 1.83 | 2.622 | 2.728 | 15 |
| 4-F-$C_4H_4$ | {CO, $H_2O$} | 2.119 | 1.851 | 1.999 [b], 2.999 [c] | 2.649 | 16 |
| Ph | 2 $PhCO_2H$ [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–$OH_2$ distance; [d] There exist two intramolecular hydrogen bonds between $PhCO_2H$ and one bridging PhCOO ligand; [e] Oxygen atoms of the neighboring bridging carboxylates coordinate with the Ru atoms in axial positions.

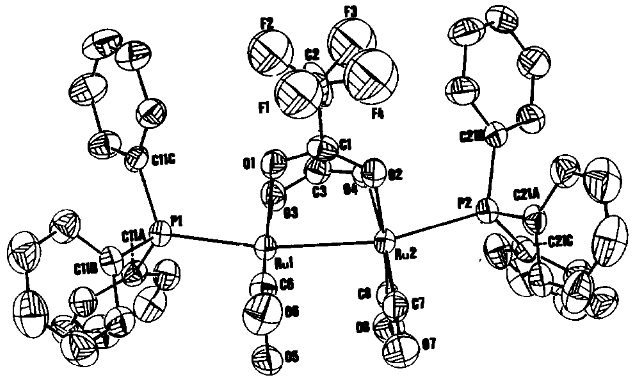

Fig. 3. ORTEP drawing of $[Ru_2(O_2CCF_3)_2(CO)_4(PPh_3)_2]$ (3) with the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

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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