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Syntheses and Structures of Ruthenium(I) Phosphinate Bridged Dimers

Christopher M. Barnes, D. Scott Bohle,* and Sara K. Madsen

Department of Chemistry, University of Wyoming,
Laramie, Wyoming 82071-3838

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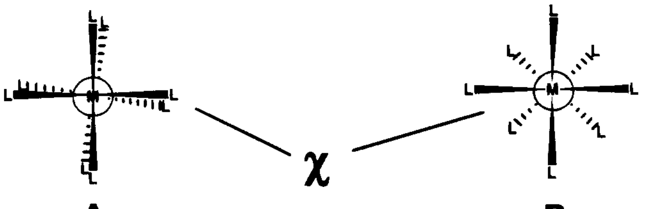
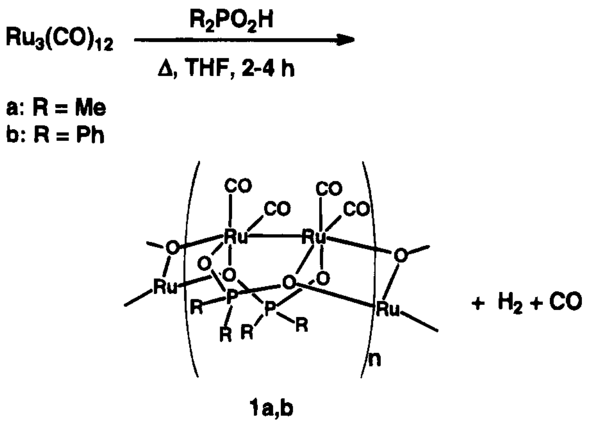
Although dimeric metal complexes with single, double, or triple metal−metal bonds have cylindrically symmetric metal−metal bonding, and therefore have no intrinsic *electronic* preference with respect to the eclipsed (**A**) and staggered (**B**) geometries, most structurally characterized examples of this class have the eclipsed structure **A**.[1] This tendency is mostly due to the presence of multiple bridging ligands between the two metals, which constrains the configurational freedom with respect to the twist angle, χ, around the bond.[2] In the course of developing the chemistry of low-valent organotransition metal phosphinate complexes[3] we have found two examples of staggered metal−metal bonds which stand in strong contrast with many carboxylato analogues[4k−k] which have eclipsed geometries with small χ angles. Herein we report (1) the synthesis of phosphinate bridged oligomers $[Ru_2(\mu_2:\mu_2:\eta^2\text{-}O_2PR_2)_2(CO)_4]_n$ (R = Me, Ph), (2) the cleavage of these compounds with triphenylphosphine to give $[Ru_2(\mu_2:\eta^2\text{-}O_2PR_2)_2(CO)_4(PPh_3)_2]$, and (3) the structures of two of these derivatives which contain surprisingly large χ angles.

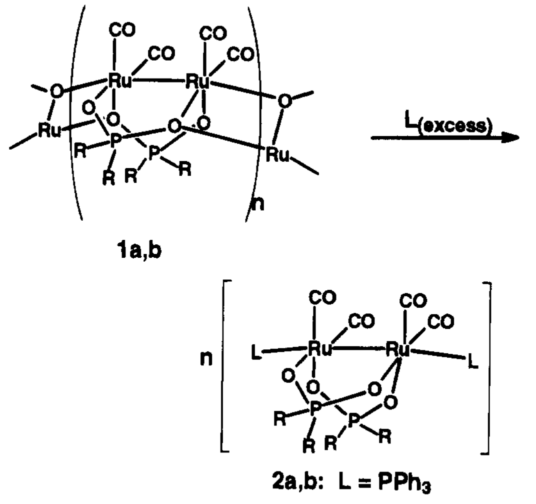


A **B**

When triruthenium dodecacarbonyl is treated with an excess of dimethylphosphinic acid in THF at reflux a copious fine yellow-orange microcrystalline precipitate forms within 2−4 h, eq 1. This material is formulated as a ruthenium(I) phosphinate bridged oligomerized dimer, $[Ru_2(\mu_2:\mu_2:\eta^2\text{-}O_2PMe_2)_2(CO)_4]_n$, **1a**, on the basis of (1) the nature of the product from the addition of Lewis bases, (2) the similarity of the IR spectrum for **1a** as contrasted with the well-known carboxylato bridged oligomer $[Ru_2\text{-}(\mu_2:\mu_2:\eta^2\text{-}O_2CCH_3)_2(CO)_4]_n$, Figure 1, and (3) elemental analysis. As with $[Ru_2\text{-}(\mu_2:\mu_2:\eta^2\text{-}O_2CCH_3)_2(CO)_4]_n$ the μ_2-oxygen that bridges the oligomerized dimers in **1a** is readily cleaved with good donor ligands such as triphenylphosphine or dimethyl sulfoxide, eq 2, to give **2a,b** in very good yields.[5]



(1)



(2)

The carbonyl stretching region of the infrared spectra of **1a** and $[Ru_2(\mu_2:\mu_2:\eta^2\text{-}O_2CCH_3)_2(CO)_4]_n$, shown in Figure 1, both contain similar manifolds above and below 2000 cm^{-1}, with the bands for **1a** being slightly shifted to lower energies for the phosphinate oligomer in **1a**. This similarity suggests that both species contain a bridged $(OC)_2Ru{-}Ru(CO)_2$ core. Strähle *et al.* have reported single crystal structures of the dimeric species $Ru_2(\mu_2:\eta^2\text{-}O_2CPh)_2(CO)_6$ and its oligomerized decarbonylation product $[Ru_2(\mu_2:\mu_2:\eta^2\text{-}O_2CPh)_2(CO)_4]_n$.[4a] This pair of well-characterized complexes illustrate a general trend in the vibrational modes for the carboxylate group, namely that both the symmetric and asymmetric carboxylate stretching bands are lower for the $\mu_2:\mu_2:\eta^2\text{-}O_2CPh$ coordination mode in the oligomer than for the $\mu_2:\eta^2\text{-}O_2CPh$ geometry in the dimer.[6] In keeping with the proposed $\mu_2:\mu_2:\eta^2\text{-}O_2PR_2$ structure in eq 1, the phosphorus−oxygen stretching bands for oligomer **1a** are also at lower energies than those for the dimeric triphenylphosphine adduct **2a**. The changes in the phosphinate stretching bands are significantly larger than for the carboxylate analogues, a trend

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(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 1st ed.; Oxford University Press: Oxford, U.K., 1982.

(2) The angle χ is defined as the average of the four unique dihedral angles that define the twist around the metal−metal bond.

(3) Bohle, D. S.; Vahrenkamp, H. A. *Inorg. Chem.* **1990**, *29*, 1097.

(4) (a) Spohn, M.; Vogt, T.; Strähle, J. *Z. Naturforsch., B* **1986**, *41*, 1373. (b) Bright, T. A.; Jones, R. A.; Nunn, C. M. *J. Coord. Chem.* **1988**, *18*, 361. (c) Bianchi, M.; Matteoli, U.; Frediani, P.; Piacenti, F.; Mardelli, M.; Pelizzi, G. *Chim. Ind. (Milan)* **1981**, *63*, 475. (d) Bulllitt, J. G.; Cotton, F. A. *Inorg. Chim. Acta* **1971**, *5*, 406. (e) Bianchi, M.; Frediani, P.; Mardelli, M.; Pelizzi, G. *Acta Crystallogr., A* **1981**, *37*, C236. (f) Rotem, M.; Goldberg, I.; Shmueli, U.; Shvo, Y. *J. Organomet. Chem.* **1986**, *314*, 185. (g) Rotem, M.; Shvo, Y.; Goldberg, I.; Shmueli, U. *Organometallics* **1984**, *3*, 1758. (h) Rotem, M.; Goldberg, I.; Shvo, Y. *Inorg. Chim. Acta* **1985**, *97*, L27. (i) Schumann, H.; Opitz, J.; Pickardt, J. *J. Organomet. Chem.* **1977**, *128*, 253. (j) Süss-Fink, G.; Wolfender, L.-L.; Neumann, F.; Stoeckli-Evans, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 429. (k) Sherlock, S. J.; Cowie, M.; Singleton, E.; Steyn, M. M. d. V. *Organometallics* **1988**, *7*, 1663. (l) Hilts, R. W.; Sherlock, S. J.; Cowie, M.; Singleton, E.; Steyn, M. M. d V. *Inorg. Chem.* **1990**, *29*, 3161. (m) Shiu, K.-B.; Peng, S.-M.; Cheng, M.-C. *J. Organomet. Chem.* **1993**, *452*, 143. (n) Cabeza, J. A.; Fernández-Colinas, J. M. *Coord. Chem. Rev.* **1993**, *126*, 319. (o) Rheinwald, G.; Stoekli-Evans, H.; Süss-Fink, G. *J. Organomet. Chem.* **1992**, *441*, 295−308.

(5) Crooks, G. R.; Johnson, B. F. G.; Lewis, J.; Williams, I. G.; Gamlen, G. *J. Chem. Soc. A* **1969**, 2761.

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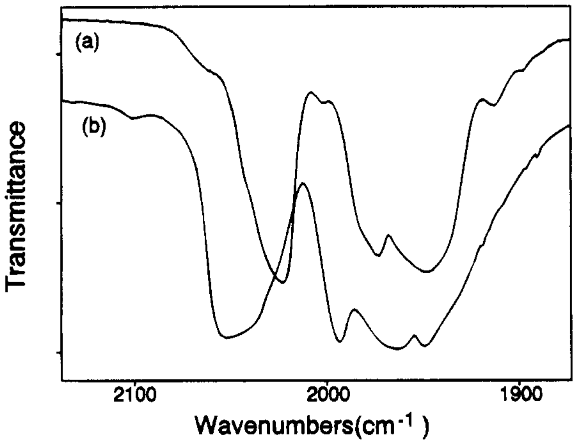

Figure 1. Carbonyl stretching regions in the IR (KBr): (a) $[Ru_2(\mu_2{:}\mu_2{:}\eta^2\text{-}O_2PMe_2)_2(CO)_4]_n$, **1a**, with peaks at 2023, 1973, and 1948 cm^{-1}; (b) $[Ru_2(\mu_2{:}\mu_2{:}\eta^2\text{-}O_2CMe)_2(CO)_4]_n$, with peaks at 2052, 1993, 1963, and 1949 cm^{-1}.

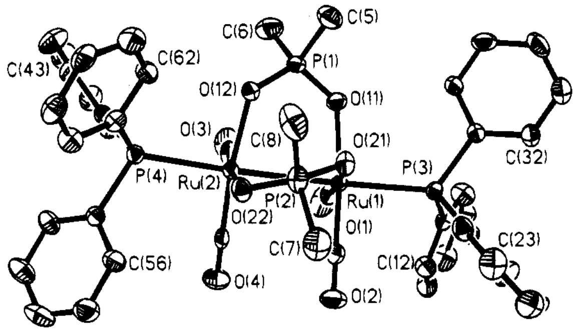

Figure 2. ORTEP plot of 2a showing all non-hydrogen atoms.

due to the lower energy of these modes and greater mixing with metal−oxygen and other modes.

The microcrystalline precipitate of **1a** has a well-defined powder diffraction pattern out to 70° in 2θ with Cu Kα radiation and has been indexed as a monoclinic unit cell with a = 18.0977(4) Å, b = 9.0756(3) Å, c = 10.0355(3) Å, β = 112.0441(2)°, and V = 1527.81(3) Å^3. Moreover, the experimental density, ϱ = 2.07 ± 0.01 g mL^{-1}, is consistent with four $Ru_2(O_2PMe_2)_2(CO)_4$ units per cell.

The dimeric ruthenium(I) species **2a,b** have been structurally characterized by single crystal X-ray diffraction; important metric parameters are collected in Table 1, and atomic coordinates are presented in Tables 2 and 3. The ORTEP views shown in Figures 2 and 3 illustrate the staggered geometry (**B**) found for both **2a** and **2b**, χ = 26.1° and χ = 22.0°, respectively, for the Ru−Ru bond. The structure of the diphenylphosphinate derivative **2b** was determined first and the twist was initially attributed to the steric interactions between the phenyl groups. Surprisingly, the structure of the dimethyl derivative **2a** proved to have an even larger twist. Clearly, steric effects of the phosphinate substituents alone do not determine χ.

The structurally characterized diruthenium(I) dicarboxylate dimers are a diverse set of compounds with a range of axial ligands, *e.g.* carbonyl,[4l] tertiary phosphine,[4i,m] and aquo,[4h] and bridging carboxylato groups, *e.g.* acetate,[4a,b,l] 4-fluorobenzoate,[4f,h] tartrate,[4j] and trifluoroacetate,[4m] that vary enormously in their steric and electronic effects. Together they form the most extensively studied subset of the sawhorse class of ruthenium(I) anion bridged dimers which also include numerous N atom donors[4n] and a sulfinato complex.[4o] Some of these compounds have χ values near zero,[4a−c] but several have larger twists ranging from 6 to 18°.[4c,f−i] Despite this significant structural variation, we find no direct correlation between the character

Table 1. Selected Interatomic Distances and Angles for $Ru_2(\mu_2{:}\eta^2\text{-}O_2PR_2)_2(CO)_4(PPh_3)_2$

Interatomic Distances (Å)[a]

	2a (R = Me)	**2b** (R = Ph)
Ru(1)−Ru(2)	2.781(1)	2.815(1)
Ru(2)−O(12)	2.126(5)	
Ru(1)−O(11)	2.140(5)	2.147(4)
Ru(2)−O(22)	2.117(8)	
Ru(1)−O(21)	2.128(8)	2.129(5)
Ru(2)−C(3)	1.847(12)	
Ru(1)−C(1)	1.846(12)	1.832(7)
Ru(2)−C(4)	1.846(8)	
Ru(1)−C(2)	1.824(8)	1.843(7)
Ru(2)−P(4)	2.443(2)	
Ru(1)−P(3)	2.461(2)	2.444(2)

Nonbonded Interatomic Distances (Å)

	2a (R = Me)	**2b** (R = Ph)
O(11)···O(12)	2.551	2.580
O(21)···O(22)	2.571	

Bond Angles (deg)

	2a (R = Me)	**2b** (R = Ph)
P(3)−Ru(1)−Ru(2)	175.8(1)	166.5(1)
Ru(1)−Ru(2)−P(4)	171.4(1)	
O(11)−Ru(1)−O(21)	86.9(2)	83.4(2)
O(12)−Ru(2)−O(22)	83.8(2)	
C(1)−Ru(1)−C(2)	90.1(4)	88.1(3)
C(3)−Ru(2)−C(4)	87.5(5)	
O(11)−P(1)−O(12)	114.4(3)	117.3(3)
O(21)−P(2)−O(22)	115.9(4)	

Dihedral Angles[b] (deg)

	2a (R = Me)	**2b** (R = Ph)
O(11)−Ru(1)−Ru(1a)−O(21a)		20.0
O(11)−Ru(1)−Ru(2)−O(12)	28.6	
O(21)−Ru(1)−Ru(2)−O(22)	25.1	

[a] Compound **2b** crystallizes in the space group *C*2/*c* and has a crystallographically imposed 2-fold rotation axis orthogonal to the metal−metal bond. As a consequence, only a single metrical parameter is given for **2b**, while for **2a**, which crystallizes in the triclinic space group *P*1, both parameters are given. [b] Absolute values of the dihedral angles.

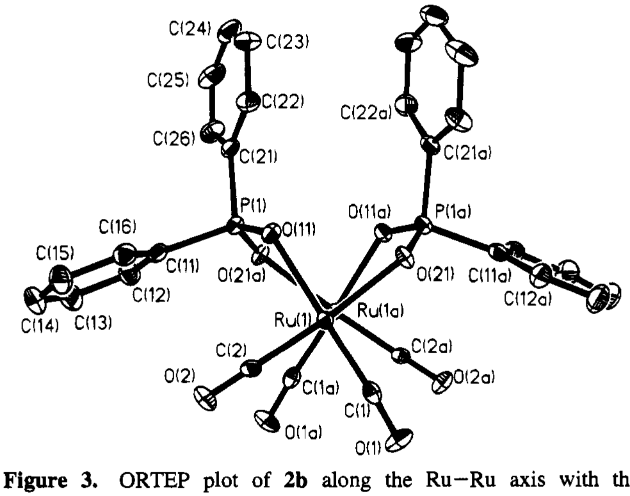

Figure 3. ORTEP plot of **2b** along the Ru−Ru axis with the triphenylphosphine ligands omitted.

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(6) Both the carboxylate and phosphinate complexes have Δ values (=$\nu_{asym} - \nu_{sym}$) which are consistent with the chelate binding of these ligands. The net lowering of these bands upon formation of the second M−O bond to one of the oxygens has been discussed in: Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227. Süss-Fink, G.; Herrmann, G.; Morys, P.; Ellermann, J.; Veit, A. *J. Organometal. Chem.* **1985**, *284*, 263.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for **2a**

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)^a
Ru(1)	8623	2546	7415	27(1)
Ru(2)	7403(1)	1881(1)	9259(1)	28(1)
P(1)	10753(3)	−836(2)	8612(1)	36(1)
P(2)	6221(3)	669(3)	7832(1)	41(1)
P(3)	9705(3)	2947(3)	5768(2)	28(1)
P(4)	6241(3)	999(3)	10805(2)	31(1)
O(11)	10808(7)	533(7)	7838(4)	41(2)
O(12)	9081(7)	−517(6)	9178(3)	38(2)
O(21)	7738(8)	864(7)	7235(3)	41(3)
O(22)	5776(7)	1241(7)	8745(4)	42(3)
C(1)	9445(12)	3885(10)	7679(6)	38(4)
C(2)	6692(11)	4252(10)	7155(6)	42(4)
C(3)	8949(12)	2403(11)	9605(5)	43(4)
C(4)	5992(12)	4012(10)	9186(5)	42(4)
O(1)	9927(11)	4724(9)	7848(5)	79(4)
O(2)	5494(8)	5335(8)	6989(5)	74(3)
O(3)	9891(10)	2723(10)	9817(5)	72(4)
O(4)	5165(10)	5320(7)	9149(5)	75(3)
C(5)	11350(12)	−2590(10)	8133(6)	56(4)
C(6)	12221(12)	−1231(12)	9377(7)	66(5)
C(7)	4460(12)	1754(14)	7209(7)	74(6)
C(8)	6592(14)	−1378(12)	7993(7)	75(6)
C(11)	10186(10)	4724(9)	5523(5)	30(3)
C(12)	8962(12)	6186(9)	5651(6)	46(4)
C(13)	9320(15)	7511(11)	5581(6)	57(5)
C(14)	10902(18)	7364(12)	5409(8)	69(6)
C(15)	12140(16)	5947(13)	5278(9)	71(6)
C(16)	11801(14)	4613(11)	5320(7)	52(5)
C(21)	8239(11)	3428(10)	4938(5)	32(3)
C(22)	7385(11)	2453(12)	5069(6)	43(4)
C(23)	6269(13)	2730(13)	4457(7)	60(5)
C(24)	6011(15)	3969(14)	3727(8)	71(6)
C(25)	6859(15)	4942(13)	3575(8)	62(5)
C(26)	7956(12)	4681(11)	4185(6)	55(5)
C(31)	11551(10)	1403(8)	5294(5)	30(3)
C(32)	11897(14)	1349(12)	4350(6)	48(4)
C(33)	13318(15)	189(13)	4017(7)	64(5)
C(34)	14402(13)	−911(12)	4600(7)	61(5)
C(35)	14079(11)	−904(11)	5548(7)	58(4)
C(36)	12657(10)	261(10)	5883(5)	41(3)
C(41)	7523(11)	513(9)	11728(6)	32(3)
C(42)	7955(13)	−930(11)	12359(6)	53(4)
C(43)	9031(15)	−1285(13)	13000(7)	72(6)
C(44)	9691(15)	−235(16)	13042(8)	66(6)
C(45)	9253(13)	1222(12)	12460(6)	55(5)
C(46)	8156(13)	1585(11)	11812(7)	47(4)
C(51)	4285(10)	2528(9)	11181(6)	34(3)
C(52)	3922(12)	2981(11)	12035(7)	42(4)
C(53)	2416(13)	4179(12)	12264(8)	56(5)
C(54)	1252(12)	4907(12)	11645(9)	65(5)
C(55)	1588(12)	4428(11)	10795(7)	60(4)
C(56)	3072(11)	3265(10)	10565(6)	47(4)
C(61)	5734(10)	−743(10)	10961(5)	34(3)
C(62)	6943(11)	−2097(9)	10610(6)	44(4)
C(63)	6618(15)	−3463(11)	10738(7)	60(5)
C(64)	5156(14)	−3510(11)	11207(7)	50(4)
C(65)	4007(15)	−2178(13)	11529(7)	54(5)
C(66)	4257(12)	−799(11)	11413(7)	45(4)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates ($\times 10^5$) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for **2b**

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)^a
Ru(1)	5677(2)	85639(4)	29096(2)	180(1)
P(1)	3990(7)	71548(11)	16686(8)	220(5)
O(11)	7021(17)	72774(29)	23923(20)	244(14)
O(21)	1939(17)	76349(31)	35481(21)	259(14)
C(1)	3605(26)	96632(48)	32883(32)	274(22)
O(1)	2333(21)	103829(35)	35027(26)	420(18)
C(2)	9012(25)	92939(44)	23216(31)	232(20)
O(2)	11047(20)	97453(34)	19522(24)	388(17)
P(2)	14599(7)	82494(11)	37472(8)	201(5)
C(11)	8766(26)	75842(44)	11224(33)	261(21)
C(12)	6362(31)	79304(49)	4900(35)	364(25)
C(13)	10031(37)	82900(59)	747(43)	524(32)
C(14)	16145(37)	83001(58)	2900(46)	541(33)
C(15)	18555(32)	79534(56)	9149(42)	458(30)
C(16)	14899(28)	75911(48)	13364(37)	332(23)
C(21)	2900(27)	59168(45)	15046(33)	274(22)
C(22)	5446(33)	52409(50)	19738(39)	410(26)
C(23)	4216(38)	42785(55)	18516(47)	539(33)
C(24)	573(35)	39952(59)	12828(50)	549(34)
C(25)	−1977(36)	46483(59)	7987(48)	546(32)
C(26)	−732(32)	55960(54)	9233(37)	417(26)
C(31)	12468(25)	82664(44)	45811(31)	225(19)
C(36)	10178(26)	90956(50)	48000(33)	300(22)
C(35)	8018(27)	91139(51)	53960(33)	319(23)
C(32)	12708(26)	74503(48)	49739(31)	267(20)
C(34)	8109(28)	83006(53)	57784(34)	358(25)
C(33)	10457(29)	74905(54)	55757(33)	363(24)
C(41)	21000(24)	90499(42)	38366(30)	219(19)
C(42)	24013(27)	93543(47)	44602(33)	309(22)
C(43)	29148(30)	98969(51)	45045(39)	393(25)
C(44)	31340(31)	101134(51)	39280(40)	396(26)
C(45)	28433(29)	98156(51)	33110(38)	373(24)
C(46)	23244(26)	92841(50)	32623(35)	318(22)
C(51)	17919(26)	70805(43)	36876(29)	229(20)
C(52)	24088(27)	69438(48)	37659(33)	292(22)
C(53)	26313(29)	60322(53)	37155(35)	358(24)
C(54)	22568(32)	52728(53)	36049(34)	388(25)
C(55)	16423(31)	53868(49)	35429(36)	352(24)
C(56)	14155(27)	63022(45)	35782(31)	289(21)
O(60)	17304(88)	16466(91)	27420(63)	2335(102)
C(61)	17577(50)	26459(74)	25838(53)	779(44)
C(62)	15878(44)	31566(50)	30694(40)	524(33)
C(63)	13867(54)	25997(87)	35151(62)	1009(56)
C(64)	16133(47)	16168(61)	34348(51)	676(40)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

of the ligands, either terminal or bridging, and the degree of dihedral twist they display. Hilts *et al.* have reported the structure of a related compound, $Ru_2(\mu_2{:}\eta^2\text{-}S_2PMe_2)_2(CO)_4(PPh_3)_2$, which possesses a χ angle of 39.1° and sulfur−sulfur distances of 3.444 and 3.445 Å.[7] These values are all unusually large and suggest that these distances are related to the dihedral twist. Although the sulfur−sulfur bites are larger than the ruthenium−ruthenium bond length, all of the structurally characterized dicarboxylate and diphosphinate bridged diruthenium(I) dimers have ruthenium−ruthenium bonds longer than their oxygen−oxygen bite distances. Thus, it does not appear that dihedral twist is imposed to improve the fit between the bridging ligands and the ruthenium−ruthenium core.

Electrophiles such as iodine, protic acids, and nitrosonium salts readily oxidatively add to the ruthenium(I) centers in **2a,b** to give a mixture of mononuclear products, as ascertained by ^{31}P NMR spectroscopy. When the reaction between **2b** and excess trifluoroacetic acid is monitored by NMR, the resulting spectrum is consistent with $[Ru_2(\mu_2\text{-}H)(\mu_2{:}\eta^2\text{-}O_2CCF_3)(\mu_2{:}\eta^2\text{-}O_2PR_2)(CO)_4(PPh_3)_2]^+$, **3a,b**, a cationic hydrido-bridged dimer with a single phosphinate bridge.[8] Unfortunately this product decomposes during workup even under dry oxygen-free conditions. This complex is less stable than the related osmium complexes $[Os_2(\mu_2\text{-}H)(\mu_2{:}\eta^2\text{-}O_2CCH_3)_2(CO)_4(L)_2]^+$, L = py or PR_3, one of which has been structurally characterized (L = PMe_2Ph), and are stable in the presence of excess trifluoroacetic

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(7) Hilts, R. W.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 3349.

(8) Important NMR data for **3a,b** ($CDCl_3$) are as follows. **3a** ^1H δ: −11.31 (dt, $^2J\{H{-}PPh_3\} = 43.1$, $^3J\{H{-}O_2PMe_2\} = 7.3$, 1, Ru−*H*−Ru). **3b** ^1H δ: −11.26 (dt, $^2J\{H{-}PPh_3\} = 43.3$, $^3J\{H{-}O_2PPh_2\} = 8.8$, 1, Ru−*H*-Ru). $^{31}P\{^1H\}$ δ: 55.18 (t, $^2J_{P-P} = 23.2$, $O_2\mathit{P}Me_2$), 33.26 (d, $\mathit{P}Ph_3$).

acid.[9] The relative lability of the phosphinate ligands in **2a,b** is further illustrated by the contrast with the reactivity of the dimethyldithiophosphinate complex $Ru_2(\mu_2:\eta^2\text{-}S_2PMe_2)_2(CO)_4(PPh_3)_2$ which can be reversibly protonated without either decomposition or loss of the bridging ligands.[7] Thus the relative lability of the phosphinate bridges in **2a,b** suggest that they may be useful synthons for the $[Ru_2(CO)_4L_2]$ fragment.

Experimental Section

Materials. The triruthenium dodecacarbonyl, diphenylphosphinic acid, and triphenylphosphine were obtained commercially (Aldrich) and used without further purification. Dimethylphosphinic acid was prepared from tetramethyldiphosphine disulfide.[10] Complex **2b** was prepared by literature methods.[3] Where noted, solvents were dried and degassed by standard techniques, but were generally used without further purification. All IR spectra were recorded on a MIDAC FTIR as either a potassium bromide pellet or as a dichloromethane solution between sodium chloride plates. The diffuse reflectance spectrum of **1a** was acquired on a Perkin-Elmer Lambda-9 spectrometer fitted with a 60 cm integrating sphere and measured against an analytical grade barium sulfate standard. Elemental microanalysis for carbon and hydrogen was performed by Desert Analytics.

Preparation of New Compounds. $[Ru_2(\mu_2:\mu_2:\eta^2\text{-}O_2PMe_2)_2(CO)_4]_n$, 1a, and $Ru_2(\mu_2:\eta^2\text{-}O_2PMe_2)_2(CO)_4(PPh_3)_2$, 2a. $Ru_3(CO)_{12}$ (164 mg) was treated with Me_2PO_2H (330 mg) and 25 mL of THF. The mixture was heated at reflux for 5 h. At this point, **1a** could be isolated in 93% yield by cooling and filtering the mixture. Anal. Calcd for $C_8H_{12}O_8P_2Ru_2\cdot{}^1/_4THF$: C, 20.86; H, 2.72. Found: C, 20.56; H, 2.72. Solvate was confirmed by ^1H NMR. IR, cm^{-1}(KBr): ν(C−O) 2023, 1973, 1948; $\nu(P{-}O)_{sym}$ 1108; $\nu(P{-}O)_{asym}$ 1019. UV−vis (KBr): λ_{max} 512 nm.

Preparation of 2a. Instead of isolating **1a**, we added triphenylphosphine (225 mg) to the above mixture and heated the resultant mixture at reflux for an additional 2 h. After removal of solvent in vacuo, IR spectra of the solid indicated that it was a mixture of **2a** and $Ru_3(CO)_9(PPh_3)_3$. The product was recrystallized twice from CH_2Cl_2/cyclohexane, rejecting the deep maroon crystals of $Ru_3(CO)_9(PPh_3)_3$ that first formed. Yield: 156 mg of **2a** (39.6%) as yellow microcrystals. Anal. Calcd for $C_{44}H_{42}O_8P_4Ru_2$: C, 51.57; H, 4.13. Found: C, 51.48; H, 4.01. NMR ($CDCl_3$): ^1H δ 7.68−7.31 (m, 30, PC_6H_5), 1.04 (d, $^2J_{P-H}$ = 6.8, 6, PCH_3), 0.93 (d, $^2J_{P-H}$ = 7.3, 6, PCH_3); $^{31}P\{^1H\}$ δ 12.78 (t, $^3J_{P-P}$ = 24.4, PPh_3), 69.4 (t, O_2PMe_2). IR, cm^{-1}(KBr): ν(C−O) 2018.0 m, 1976.0 w, 1936.0 m, 1908.5 w; $\nu(P{-}O)_{sym}$ 1240 s; $\nu(P{-}O)_{asym}$ 1131 s. Single crystals suitable for X-ray diffraction were grown by slow evaporation of a solution of diethyl ether.

X-ray Crystallography. Single Crystal. General experimental details for X-ray data collection have been described before.[11] The structures were solved by direct methods (**2a**) or Patterson techniques (**2b**) and refined by full-matrix least-squares techniques. Important single crystal X-ray diffraction parameters are collected in Table 4.

Table 4. Crystallographic Data for $Ru_2(\mu_2:\eta^2\text{-}O_2PR_2)_2(CO)_4(PPh_3)_2$

	2a	**2b**
formula	$C_{44}H_{42}O_8P_4Ru_2$	$C_{72}H_{66}O_{10}P_4Ru_2$
a (Å)	8.975(2)	22.885(4)
b (Å)	9.365(2)	14.112(5)
c (Å)	14.929(3)	20.265(4)
α (deg)	76.09(3)	
β (deg)	78.71(3)	100.59(1)
γ (deg)	64.95(3)	
V (Å^3)	1097(4)	6433(3)
Z	1	4
fw	1024.8	1417.3
space group	$P1$	$C2/c$
T (°C)	23	−100
λ (Å)	0.710 73	0.710 73
ϱ_{calc} (g cm^{-3})	1.551	1.463
μ(Mo Kα_1) (mm^{-1})	0.885	0.615
R^a	0.028	0.044
$R_w{}^a$	0.031	0.054

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

$Ru_2(\mu_2:\eta^2\text{-}O_2PMe_2)_2(CO)_4(PPh_3)_2$, 2a. Data were collected at 23 °C on a crystal of dimensions 0.24 × 0.15 × 0.07 mm. The compound crystallized in the noncentrosymmetric triclinic space group $P1$, with one molecule in a cell of dimensions a = 8.975(2) Å, b = 9.365(2) Å, c = 14.929(3) Å, α = 76.09(3)°, β = 78.71(3)°, γ = 64.95(3)°, and V = 1097.1(4) Å^3. A total of 4145 independent reflections were gathered, the octants collected being $+h,\pm k,\pm l$ using the Wyckoff scan method. The structure has been refined to conventional R factor values of R = 0.0281 and R_w = 0.0306 on the basis of 3517 observed reflections with $I > 6\sigma(I)$ in the 2θ range 4−50°, giving a data to parameter ratio of 6.8:1. All non-hydrogen atoms were refined anisotropically; the $P{-}CH_3$ hydrogen atoms, located in the Fourier map, were refined isotropically, while the $P{-}C_6H_5$ hydrogen atoms were placed at idealized positions. The maximum and minimum residual densities remaining were 0.56 and −0.41 e Å^{-3}, respectively. Selected metrical data and atomic positions are presented in Tables 1 and 2.

$[Ru_2(\mu_2:\eta^2\text{-}O_2PPh_2)(CO)_4(PPh_3)_2]\cdot 2C_4H_8O$, 2b. Data were collected at −100 °C on a crystal of dimensions 0.22 × 0.20 × 0.58 mm^3. The compound crystallized in the centrosymmetric monoclinic space group $C2/c$ with four molecules in a cell of dimensions a = 22.885(4) Å, b = 14.112(5) Å, c = 20.265(4) Å, β = 100.59(1)°, and V = 6433(3) Å^3. A total of 5678 independent reflections were gathered, the octants collected being $-h,+k,\pm l$ using the $2\theta{-}\theta$ scan method. The structure has been refined to conventional R factor values of R = 0.0445 and R_w = 0.0541 on the basis of 3592 observed reflections with $I > 6\sigma(I)$ in the 2θ range 4−50°, giving a data to parameter ratio of 9.0:1. The compound crystallized with one THF solvate per Ru asymmetric unit. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms located in the Fourier map were refined isotropically. The hydrogen atoms of the solvate were placed in fixed calculated positions (C−H = 0.96 Å). The maximum and minimum residual densities remaining were 0.56 and −1.24 e Å^{-3}, respectively. Selected metrical data and atomic positions are presented in Tables 1 and 3.

Powder: Crystal Data for 1a. The X-ray powder pattern of $[Ru_2(O_2PMe_2)_2(CO)_4]_n$ was recorded on a Scintag powder diffractometer at 25 °C with Cu Kα_1 radiation (λ = 1.5405 98 Å) and microcrystalline quartz used as an external standard. The powder pattern was indexed using the program TREOR92,[12] to give a monoclinic cell with a = 18.097 Å, b = 9.076 Å, c = 10.034 Å, β = 112.0°, and V = 1527 Å^3. From the indexed powder pattern the unit cell parameters were refined by a least-squares procedure. The values obtained in the refinements were a = 18.0977(4) Å, b = 9.0756(3) Å, c = 10.0355(3) Å, β = 112.0441(2)°, and V = 1527.81(3) Å^3 using 52 lines of the pattern. The density of the crystallites was determined to be ϱ = 2.07 ± 0.01 g mL^{-1} by flotation in carbon tetrachloride and dibromoethane, thus establishing that there are four $Ru_2(O_2PMe_2)_2(CO)_4$ units per cell (Z = 4).

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Supplementary Material Available: For **2a,b**, tables giving summaries of the X-ray crystallographic experimental details, hydrogen positional and isotropic thermal parameters, anisotropic thermal parameters, and bond distances and angles (14 pages). Ordering information is given on any current masthead page.

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