

The crystal structure of bis(triphenylphosphine)decacarbonyl-triruthenium, $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$. An example of unsymmetrical semibridging carbonyls in a substituted cluster

Tyrena Chin-Choy, Nancy L. Keder, Galen D. Stucky and Peter C. Ford*

Department of Chemistry, University of California, Santa Barbara, Santa Barbara, California 93106 (U.S.A.)

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Abstract

The crystal structure of the disubstituted cluster, $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$, prepared from $\text{Ru}_3(\text{CO})_{12}$ and PPh_3 , was determined by single crystal X-ray diffraction methods. The crystals are orthorhombic, space group $P2_12_12_1$ with a 14.851(2), b 17.039(3), c 34.693(5) Å, and $Z = 8$. The structure was refined to R 8.2% for 4616 observed reflections. The cluster consists of a triangle of Ru atoms with the PPh_3 ligands equatorially bonded to different Ru atoms and approximately *trans* to one of the Ru–Ru bonds. The configuration of the four carbonyls on the unique ruthenium is substantially twisted from that found for the $\text{Ru}(\text{CO})_4$ group of $\text{Ru}_3(\text{CO})_{12}$. This configuration allows a semibridging orientation of several carbonyls, attributed to both the steric and electronic effects of the PPh_3 substitution.

Introduction

In the course of studies of the reactions and properties of metal clusters, the crystal structure of the disubstituted cluster, $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$, was determined by X-ray diffraction techniques. For this structure, it was found that the orientation of the carbonyls had adopted a geometry different from that of the parent complex $\text{Ru}_3(\text{CO})_{12}$. Described here are these results, and comparisons to the structure of other substituted triruthenium carbonyl clusters recalculated from published parameters.

Experimental

Preparation of $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$

The disubstituted cluster was prepared by Alan Friedman from $\text{Ru}_3(\text{CO})_{12}$ and PPh_3 via the procedure described by Bruce et al. [1] and was recrystallized from THF/hexane via the solvent diffusion technique.

Table 1

Cell and data collection parameters for $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$

crystal dimension, mm	(triangular prism) 0.30 × 0.33 × 0.37 × 0.35	transmission factors	
		max	0.7936
crystal color	dark red	min	0.7312
space group	$P2_12_12_1$	scan rate deg./min	3.0
Z	8	scan range	
radiation type, λ Å	Mo- K_{α} , 0.7107	below K_{α_1}	0.9
(calc'd) g/cm ³	1.68	above K_{α_2}	1.0
(obs'd) g/cm ³	1.61(1)	2 θ limits	
temperature	296 K	min	0.0
V, mm ³ (of crystal)	0.03911	max	50
abs. coeff., μ cm ⁻¹	11.266	total meas'd data	8505
a, Å	14.851(2)	data collected	+ h, + k, + l
b, Å	17.039(3)	systematic absences	
c, Å	34.693(5)	(h00)	$h = 2n + 1$
$\alpha = \beta = \gamma$	90°	(0k0)	$k = 2n + 1$
scan mode	$\theta/2\theta$	(00l)	$l = 2n + 1$
		no. of parameters refined	441
		R	0.082
		R _w	0.092
		error of fit	2.23
		no. of reflections ($I > 3\sigma(I)$)	4616

X-Ray data collection

The crystal of $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$ was mounted on a glass fiber with epoxy. A Blake Industries four-circle diffractometer [2*] interfaced to a DEC micro-VAX II computer with stepping motor controllers from Crystal Logic was used to obtain the diffraction data. The cell constants and other crystallographic data are reported in Table 1. Three standard reflections were measured every 97 reflections and showed no appreciable decay. An absorption correction using the numerical integration method was applied [3].

Solution and refinement of the structure

Inspection of the intensity data revealed the systematic absences $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$; consistent with the space group $P2_12_12_1$ **. The unit cell contains eight molecules; there are two molecules in the asymmetric unit. The ruthenium and phosphorus atoms were located by direct methods (MULTAN 80). The carbonyl and phenyl ligands were found by successive cycles of full-matrix least squares refinement and Fourier syntheses [4*].

In order to maximize the data to parameter ratio, the phenyl rings of the triphenylphosphine ligands were refined with idealized geometries [5]. Parameters corresponding to the C–C distances of the phenyl rings were refined [6*]; the C–H distance was fixed at 0.95 Å the elements of the group translational vibration tensor,

* This and other references marked with asterisks indicate notes occurring in the list of references.

** The space group has inherent chirality, which is independent of the molecule itself. To test the chirality of the structure, the coordinates were inverted and the structure was allowed to refine. The assignment of the absolute configuration, based on the R-factor ratio test, is reported here.

T , and the diagonal elements of the group librational vibration tensor, L , were refined [7]. Carbonyls (08) and (51) were refined with idealized geometry (C–O 1.17 Å). Individual positional parameters for all other atoms, i.e. ruthenium, phosphorus and carbon and oxygen of other carbonyls, were refined. Anisotropic thermal parameters were refined for the Ru atoms and the P atoms. Individual isotropic thermal parameters were refined for all C and O atoms of the carbonyl ligands. The largest features in the final difference map were three peaks of height 1.2, 1.1 and 0.9 e/Å³ located near the Ru atoms, Ru(1), Ru(3) and Ru(6). The refinement converged at R 0.082 and R_w 0.092 *; the error of fit was 2.23.

Results

The asymmetric unit of the crystal is composed of two molecules, A and B, as seen in Fig. 1. The unit cell is depicted in Fig. 2.

Table 2 contains atomic positional parameters with estimated standard deviations from the final cycle of least-squares refinement. Tables 3 and 4 contain, respectively, selected bond angles and distances for the structure.

Discussion

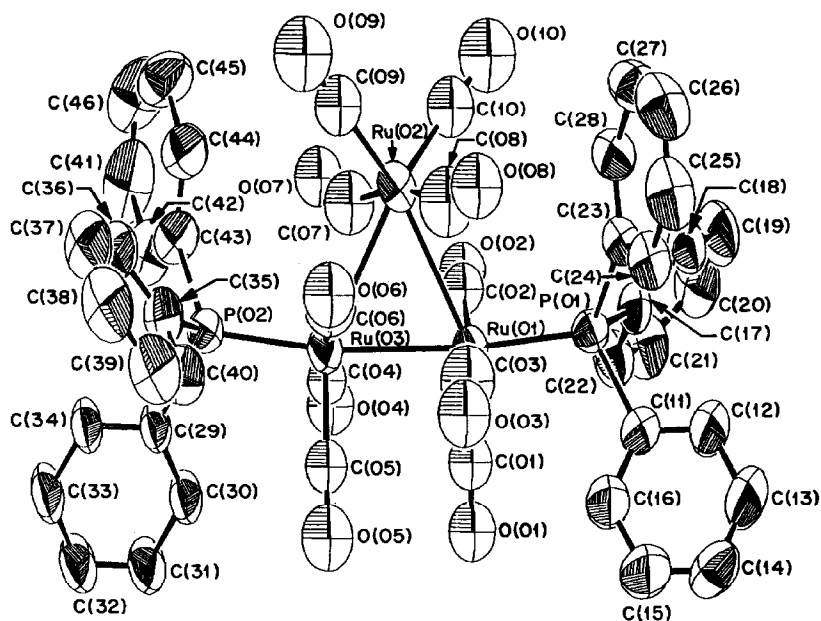
Molecules A and B have generally the same features, yet there are some differences. The main focus of this discussion will be on molecule A; however, differences between molecule A and B will be discussed below.

Molecular structures A and B of Ru₃(CO)₁₀(PPh₃)₂ are each composed of a triangle of Ru atoms with the phosphine ligands equatorially bonded to two different Ru atoms. The two PPh₃'s are approximately *trans* to the same Ru–Ru bond with P–Ru–Ru bond angles close to 170° in each case (Table 3). The P–Ru–Ru–P dihedral angles are 87.5° and 90.0° in molecules A and B, respectively. The positions of carbonyl ligands are significantly distorted from the respective positions of the carbonyls found on the parent molecule, Ru₃(CO)₁₂ [8]. The three carbonyl ligands on each phosphine-substituted ruthenium lie approximately in a plane perpendicular to the Ru₃ triangle; however, these two sets of carbonyl ligands are rotated with respect to each other. A particularly interesting feature is that the Ru(CO)₄ unit of the unique ruthenium is twisted from the position this unit would occupy in the parent compound, Ru₃(CO)₁₂. The “axial” carbonyl (07) in the Ru(CO)₄ unit is therefore positioned under the Ru(02)–Ru(03) bond, while the other “axial” carbonyl (08) is positioned over the Ru(02)–Ru(01) bond. At the same time the Ru–C–O angles for both carbonyls have bent significantly from linearity to 153(3)° and 161.8° ** respectively. These orientations are clearly suggestive of “semibridging” behavior for these carbonyls [9]. Above the Ru(02)–Ru(03) bond and below the Ru(02)–Ru(01) bond, carbonyls (numbers 06 and 02 respectively) from the phosphine substituted Ru(CO)₃L units are also oriented in positions

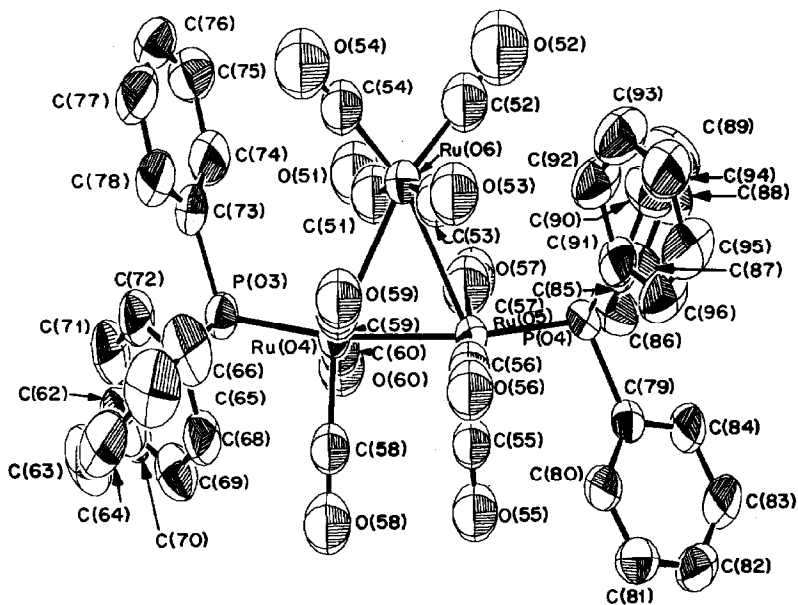
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* As a referee noted, the R -factor is rather high. This may be due to the high parameter to data ratio. There are 182 atoms in the asymmetric unit. In addition, the data was collected at room temperature, thus allowing for thermal motion.

** Estimated standard deviations which were omitted included atoms with idealized geometries, i.e. rigid bodies.



MOLECULE A



MOLECULE B

Fig. 1. Molecular structure of $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$ showing the numbering scheme (50% probability ellipsoids). Hydrogen atoms and selected labels have been omitted for clarity. Figures drawn using the program ORTEP.

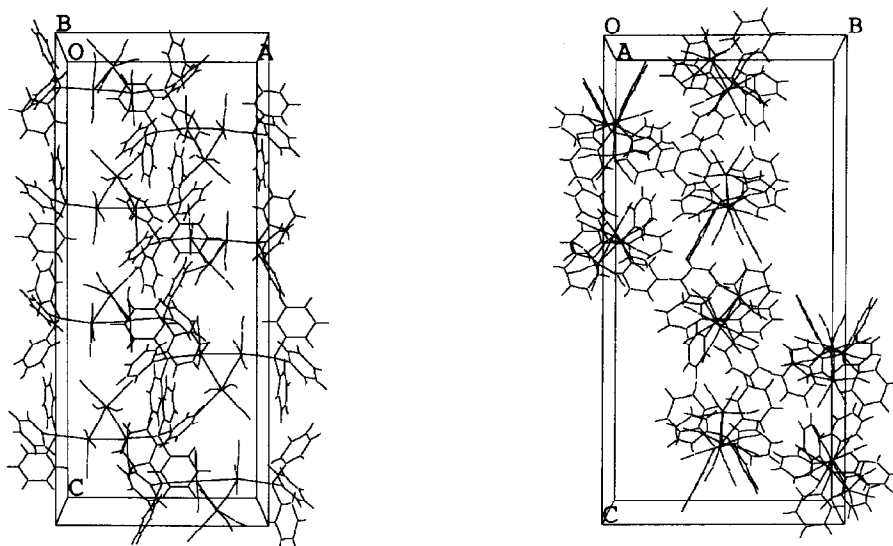


Fig. 2. Two different views of the unit cell for $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$.

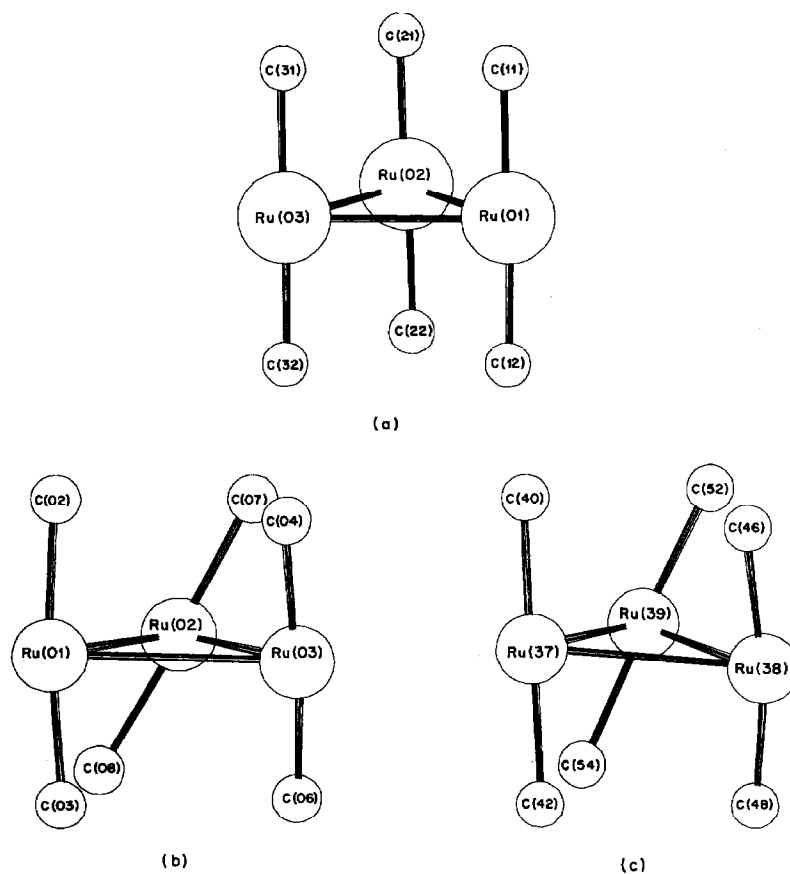


Fig. 3. Orientations of the axial carbonyls in (a) $\text{Ru}_3(\text{CO})_{12}$ (calculated from data in reference 8), in (b) $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$ (molecule A, this work), and in (c) $\text{Ru}_3(\text{CO})_{10}(\text{P}(\text{OCH}_3)_3)_2$ (calculated from data in ref. 10b); Ru(37) and Ru(38) are the $\text{P}(\text{OCH}_3)_3$ substituted metals.

Table 2

Positional parameters for atoms of Ru₃(CO)₁₀(PPh₃)₂: (includes molecule A and B)

Atom	x	y	z	Atom	x	y	z
<i>Molecule A:</i>							
Ru(1)	-0.1771(1)	-0.5100(1)	-0.3457(1)	C(11)	0.0378	-0.4392	-0.3800
Ru(2)	-0.2763(2)	-0.5050(2)	-0.2760(1)	C(12)	0.1295	-0.4348	-0.3790
Ru(3)	-0.3689(1)	-0.5176(1)	-0.3468(1)	C(13)	0.1751	-0.3995	-0.4084
P(1)	-0.0220(4)	-0.4852(4)	-0.3379(2)	C(14)	0.1289	-0.3686	-0.4388
P(2)	-0.5258(4)	-0.5354(4)	-0.3396(2)	C(15)	0.0373	-0.3730	-0.4398
C(01)	-0.1706(19)	-0.5463(16)	-0.3955(8)	C(16)	-0.0083	-0.4083	-0.4104
C(02)	-0.1730(18)	-0.6116(16)	-0.3218(7)	C(17)	0.0479	-0.5719	-0.3292
C(03)	-0.1958(24)	-0.4068(22)	-0.3580(10)	C(18)	0.1172	-0.5746	-0.3020
C(04)	-0.3521(17)	-0.6231(14)	-0.3615(7)	C(19)	0.1680	-0.6429	-0.2976
C(05)	-0.3723(18)	-0.4747(15)	-0.3965(8)	C(20)	0.1494	-0.7086	-0.3203
C(06)	-0.3777(25)	-0.4123(21)	-0.3248(10)	C(21)	0.0802	-0.7059	-0.3475
C(07)	-0.3252(23)	-0.6079(30)	-0.2849(9)	C(22)	0.0294	-0.6375	-0.3519
C(09)	-0.3609(22)	-0.4641(17)	-0.2407(9)	C(23)	0.0084	-0.4162	-0.2979
C(10)	-0.1995(21)	-0.5530(19)	-0.2425(9)	C(24)	0.0356	-0.3414	-0.3053
O(01)	-0.1635(13)	-0.5791(11)	-0.4257(5)	C(25)	0.0559	-0.2922	-0.2756
O(02)	-0.1646(13)	-0.6773(11)	-0.3152(5)	C(26)	0.0491	-0.3178	-0.2386
O(03)	-0.2072(15)	-0.3425(14)	-0.3720(6)	C(27)	0.0220	-0.3926	-0.2312
O(04)	-0.3384(13)	-0.6841(11)	-0.3733(5)	C(28)	0.0016	-0.4417	-0.2609
O(05)	-0.3743(15)	-0.4443(13)	-0.4267(6)	C(29)	-0.5856	-0.5785	-0.3818
O(06)	-0.3881(15)	-0.3452(13)	-0.3205(6)	C(30)	-0.5404	-0.6100	-0.4124
O(07)	-0.3585(13)	-0.6690(11)	-0.2745(5)	C(31)	-0.5872	-0.6424	-0.4424
O(09)	-0.4111(18)	-0.4400(15)	-0.2186(7)	C(32)	-0.6792	-0.6433	-0.4417
O(10)	-0.1465(17)	-0.5837(14)	-0.2211(7)	C(33)	-0.7244	-0.6117	-0.4111
				C(34)	-0.6776	-0.5793	-0.3811
				C(35)	-0.5936	-0.4451	-0.3315
				C(36)	-0.6581	-0.4373	-0.3036
				C(37)	-0.7053	-0.3688	-0.3003
				C(38)	-0.6881	-0.3079	-0.3249
				C(39)	-0.6236	-0.3156	-0.3528
				C(40)	-0.5764	-0.3842	-0.3561
				C(43)	-0.5560	-0.6020	-0.3002
				C(44)	-0.5484	-0.5772	-0.2626
				C(45)	-0.5677	-0.6278	-0.2329
				C(46)	-0.5945	-0.7033	-0.2408
				C(41)	-0.6020	-0.7282	-0.2783
				C(42)	-0.5828	-0.6775	-0.3080
				C(8)	-0.2331	-0.4063	-0.2809
				O(8)	-0.1918	-0.3452	-0.2733
				C(61)	-0.5743	-0.4553	-0.1300
<i>Molecule B:</i>							
Ru(4)	-0.3521(1)	-0.5114(1)	-0.0962(1)	C(62)	-0.6459	-0.4962	-0.1454
Ru(5)	-0.1595(1)	-0.5340(1)	-0.0907(1)	C(63)	-0.6909	-0.4669	-0.1770
Ru(6)	-0.2524(2)	-0.4379(1)	-0.0355(1)	C(63)	-0.6909	-0.4669	-0.1770
P(3)	-0.5099(4)	-0.4954(4)	-0.0876(2)	C(65)	-0.5929	-0.3560	-0.1778
P(4)	-0.0001(4)	-0.5285(4)	-0.0852(2)	C(66)	-0.5478	-0.3852	-0.1462
C(52)	-0.1653(22)	-0.4211(19)	0.0030(9)	C(67)	-0.5721	-0.5697	-0.0782
C(53)	-0.1977(20)	-0.3697(18)	-0.0715(8)	C(68)	-0.5479	-0.6548	-0.0992
C(54)	-0.3345(21)	-0.3615(17)	-0.0190(8)	C(69)	-0.5898	-0.7255	-0.0925
C(55)	-0.1642(18)	-0.6254(15)	-0.1186(7)	C(70)	-0.6558	-0.7310	-0.0649
C(56)	-0.1557(19)	-0.4652(16)	-0.1332(8)	C(71)	-0.6800	-0.6659	-0.0440
C(57)	-0.1716(23)	-0.5902(19)	-0.0420(9)	C(72)	-0.6382	-0.5953	-0.0506
C(58)	-0.3590(18)	-0.5602(16)	-0.1423(8)	C(73)	-0.5501	-0.4339	-0.0485
C(59)	-0.3388(22)	-0.4123(18)	-0.1178(9)	C(74)	-0.5286	-0.4569	-0.0113
C(60)	-0.3512(19)	-0.6126(16)	-0.0681(7)	C(75)	-0.5524	-0.4100	0.0196

Table 2 (continued)

Atom	x	y	z	Atom	x	y	z
O(52)	-0.1157(20)	-0.4008(16)	0.0258(8)	C(76)	-0.5976	-0.3401	0.0134
O(53)	-0.1692(15)	-0.3169(13)	-0.0868(6)	C(77)	-0.6190	-0.3171	-0.0238
O(54)	-0.3879(18)	-0.3097(15)	-0.0123(7)	C(78)	-0.5952	-0.3640	-0.0547
O(55)	-0.1623(14)	-0.6817(12)	-0.1372(6)	C(79)	0.0600	-0.5846	-0.1239
O(56)	-0.1495(14)	-0.4272(12)	-0.1599(6)	C(80)	0.0266	-0.5846	-0.1609
O(57)	-0.1692(14)	-0.6417(12)	-0.0182(6)	C(81)	0.0741	-0.6204	-0.1900
O(58)	-0.3631(15)	-0.5925(12)	-0.1727(6)	C(82)	0.1550	-0.6561	-0.1821
O(59)	-0.3320(14)	-0.3497(12)	-0.1329(6)	C(83)	0.1884	-0.6561	-0.1452
O(60)	-0.3544(15)	-0.6719(12)	-0.0551(6)	C(84)	0.1409	-0.6204	-0.1161
				C(85)	0.0461	-0.5741	-0.0408
				C(86)	0.0325	-0.6527	-0.0352
				C(87)	0.0612	-0.6876	-0.0019
				C(88)	0.1033	-0.6439	0.0259
				C(89)	0.1169	-0.5653	0.0203
				C(90)	0.0883	-0.5304	-0.0131
				C(91)	0.0540	-0.4312	-0.0878
				C(92)	0.0266	-0.3748	-0.0623
				C(93)	0.0665	-0.3024	-0.0625
				C(94)	0.1338	-0.2863	-0.0883
				C(95)	0.1612	-0.3427	-0.1139
				C(96)	0.1213	-0.4151	-0.1136
				C(51)	-0.3022	-0.5251	-0.0097
				O(51)	-0.3311	-0.5626	0.0157

toward Ru(02) along the Ru–Ru bonds. The orientations of the axial carbonyls in three related triruthenium clusters: Ru₃(CO)₁₂ [8], Ru₃(CO)₁₀(PPh₃)₂ (this work) and Ru₃(CO)₁₀(P(OCH₃)₃)₂ [10b] are illustrated in Fig. 3. It is clear from Fig. 3 that, for each of the disubstituted clusters, the Ru(CO)₄ unit has been twisted substantially, the rotation being somewhat more extensive for the triphenylphosphine derivative.

The semibridging carbonyls along the Ru(02)–Ru(03) bond of Ru₃(CO)₁₀(PPh₃)₂, molecule A, are illustrated in Fig. 4(a). These are shown to be unsymmetrical as evidenced by the Ru(02)–C(07)–O(07) angle (153(3)°) being considerably more acute than the Ru(03)–C(06)–O(06) angle (164(3)°). This semibridging behavior, as compared to the structure of Ru₃(CO)₁₂, can very likely be attributed to the greater electron donating ability of the phosphine relative to CO [9]. Thus, the more electron rich Ru(03) and Ru(01) centers can donate more electron density to the carbons of the semibridging CO(07) and CO(08), respectively, than does Ru(02) to carbonyls (02) and (06) [11]. One cannot exclude steric effects given the large size of the PPh₃ ligand. If, for example, one arbitrarily places the carbons of the Ru(CO)₄ group at sites equivalent to their positions in Ru₃(CO)₁₂, molecular graphics calculations show the oxygens of carbonyls to fall within the Van der Waals radii of the phenyl hydrogens as well as other nonbonded steric interactions. Thus, it is likely that the twisting of the Ru(CO)₄ group into a position attractive for the double semibridging has both electronic and steric origins.

From molecular graphics computations of the packed crystals, a comparison between a structure with the observed Ru(CO)₄ unit and one with the parent-like Ru(CO)₄ unit was made. These computations indicated that the Ru(CO)₄ unit was

Table 3

Selected bond angles (degrees) (esd's not listed for measurements belonging to atoms in groups treated as rigid bodies)

Molecule A:		Molecule B:	
Ru(2)–Ru(1)–Ru(3)	59.6(1)	Ru(6)–Ru(4)–Ru(5)	59.9(1)
Ru(3)–Ru(2)–Ru(1)	60.6(1)	Ru(6)–Ru(5)–Ru(4)	59.5(1)
Ru(2)–Ru(3)–Ru(1)	59.9(1)	Ru(4)–Ru(6)–Ru(5)	60.6(1)
P(1)–Ru(1)–Ru(2)	113.9(2)	P(3)–Ru(4)–Ru(5)	169.0(2)
P(1)–Ru(1)–Ru(3)	170.3(2)	P(3)–Ru(4)–Ru(6)	111.5(2)
P(2)–Ru(3)–Ru(1)	171.6(2)	P(4)–Ru(5)–Ru(4)	170.1(2)
P(2)–Ru(3)–Ru(2)	113.5(2)	P(4)–Ru(5)–Ru(6)	113.7(2)
C(01)–Ru(1)–Ru(2)	147.1(9)	C(51)–Ru(6)–Ru(4)	78.6
C(01)–Ru(1)–Ru(3)	91.4(9)	C(51)–Ru(6)–Ru(5)	93.2
C(02)–Ru(1)–Ru(2)	71.0(8)	C(52)–Ru(6)–Ru(4)	160.8(10)
C(02)–Ru(1)–Ru(3)	89.8(8)	C(52)–Ru(6)–Ru(5)	103.3(10)
C(03)–Ru(1)–Ru(2)	95.2(11)	C(53)–Ru(6)–Ru(4)	90.3(9)
C(03)–Ru(1)–Ru(3)	83.6(11)	C(53)–Ru(6)–Ru(5)	72.7(9)
C(04)–Ru(3)–Ru(1)	85.1(8)	C(54)–Ru(6)–Ru(4)	101.1(9)
C(04)–Ru(3)–Ru(2)	104.1(8)	C(54)–Ru(6)–Ru(5)	155.8(9)
C(05)–Ru(3)–Ru(1)	91.2(8)	C(55)–Ru(5)–Ru(4)	92.3(9)
C(05)–Ru(3)–Ru(2)	141.6(8)	C(55)–Ru(5)–Ru(6)	144.8(8)
C(06)–Ru(3)–Ru(1)	91.1(11)	C(56)–Ru(5)–Ru(4)	84.0(9)
C(06)–Ru(3)–Ru(2)	67.8(10)	C(56)–Ru(5)–Ru(6)	100.4(8)
C(07)–Ru(2)–Ru(1)	91.8(10)	C(57)–Ru(5)–Ru(4)	91.8(10)
C(07)–Ru(2)–Ru(3)	66.9(10)	C(57)–Ru(5)–Ru(6)	70.0(10)
C(8)–Ru(2)–Ru(1)	74.3	C(58)–Ru(4)–Ru(5)	93.1(9)
C(8)–Ru(2)–Ru(3)	101.3	C(58)–Ru(4)–Ru(6)	151.9(9)
C(09)–Ru(2)–Ru(1)	155.6(9)	C(59)–Ru(4)–Ru(5)	92.4(10)
C(09)–Ru(2)–Ru(3)	105.6(9)	C(59)–Ru(4)–Ru(6)	81.0(9)
C(10)–Ru(2)–Ru(1)	101.9(9)	C(60)–Ru(4)–Ru(5)	81.1(8)
C(10)–Ru(2)–Ru(3)	145.7(10)	C(60)–Ru(4)–Ru(6)	90.9(8)
C(01)–Ru(1)–P(1)	96.7(9)	C(58)–Ru(4)–P(3)	96.2(9)
C(02)–Ru(1)–P(1)	94.6(8)	C(59)–Ru(4)–P(3)	92.9(10)
C(03)–Ru(1)–P(1)	90.2(12)	C(60)–Ru(4)–P(3)	92.6(8)
C(04)–Ru(3)–P(2)	92.1(8)	C(55)–Ru(5)–P(4)	96.5(9)
C(05)–Ru(3)–P(2)	96.9(8)	C(56)–Ru(5)–P(4)	90.5(9)
C(06)–Ru(3)–P(2)	90.6(11)	C(57)–Ru(5)–P(4)	92.4(10)
C(01)–Ru(1)–C(02)	95.8(12)	C(52)–Ru(6)–C(51)	93.0
C(03)–Ru(1)–C(01)	96.4(14)	C(52)–Ru(6)–C(53)	94.6(13)
C(03)–Ru(1)–C(02)	166.2(14)	C(53)–Ru(6)–C(51)	165.3
C(04)–Ru(3)–C(06)	171.9(13)	C(54)–Ru(6)–C(51)	98.5
C(05)–Ru(3)–C(04)	97.3(11)	C(54)–Ru(6)–C(52)	97.2(13)
C(05)–Ru(3)–C(06)	90.0(13)	C(54)–Ru(6)–C(53)	93.1(13)
C(07)–Ru(2)–C(8)	165.3	C(55)–Ru(5)–C(56)	96.7(11)
C(09)–Ru(2)–C(07)	100.9(13)	C(55)–Ru(5)–C(57)	92.1(12)
C(09)–Ru(2)–C(8)	90.5	C(56)–Ru(5)–C(57)	170.4(12)
C(10)–Ru(2)–C(07)	86.0(14)	C(58)–Ru(4)–C(59)	93.9(13)
C(10)–Ru(2)–C(8)	101.4	C(58)–Ru(4)–C(60)	92.0(11)
C(10)–Ru(2)–C(09)	99.7(13)	C(59)–Ru(4)–C(60)	171.5(13)

Table 3 (continued)

Molecule A:		Molecule B:	
O(01)–C(01)–Ru(1)	171.4(24)	O(51)–C(51)–Ru(6)	158.7
O(02)–C(02)–Ru(1)	165.3(24)	O(52)–C(52)–Ru(6)	170.9(32)
O(03)–C(03)–Ru(1)	169.8(31)	O(53)–C(53)–Ru(6)	164.5(27)
O(04)–C(04)–Ru(3)	173.8(23)	O(54)–C(54)–Ru(6)	173.2(28)
O(05)–C(05)–Ru(3)	176.7(24)	O(55)–C(55)–Ru(5)	175.9(26)
O(06)–C(06)–Ru(3)	164.0(31)	O(56)–C(56)–Ru(5)	175.4(26)
O(07)–C(07)–Ru(2)	153.2(27)	O(57)–C(57)–Ru(5)	161.5(27)
O(8)–C(8)–Ru(2)	161.8	O(58)–C(58)–Ru(4)	179.7(26)
O(09)–C(09)–Ru(2)	178.4(29)	O(59)–C(59)–Ru(4)	177.5(28)
O(10)–C(10)–Ru(2)	177.8(28)	O(60)–C(60)–Ru(4)	173.9(25)

displaced in such a way to minimize Van der Waals interactions. In the parent-like case; where no carbonyl ligand on the Ru(CO)₄ unit was bent; it was found that Van der Waals interactions (intramolecular as well as intermolecular) occurred between two carbonyl oxygen atoms. Intermolecular interactions between carbonyl ligands on one molecule and phenyl groups on another were also observed. The

Table 4

Selected bond lengths (Å) (esd's not listed for measurements belonging to atoms in groups treated as rigid bodies)

Molecule A:		Molecule B:	
Ru(1)–Ru(2)	2.833(3)	Ru(4)–Ru(5)	2.893(3)
Ru(1)–Ru(3)	2.852(3)	Ru(4)–Ru(6)	2.863(3)
Ru(2)–Ru(3)	2.823(3)	Ru(5)–Ru(6)	2.873(3)
Ru(1)–P(1)	2.357(6)	Ru(4)–P(3)	2.378(6)
Ru(3)–P(2)	2.363(7)	Ru(5)–P(4)	2.377(7)
Ru(1)–C(01)	1.838(28)	Ru(6)–C(51)	1.885
Ru(1)–C(02)	1.920(27)	Ru(6)–C(52)	1.881(34)
Ru(1)–C(03)	1.831(37)	Ru(6)–C(53)	1.890(31)
Ru(3)–C(04)	1.885(25)	Ru(6)–C(54)	1.873(32)
Ru(3)–C(05)	1.873(27)	Ru(5)–C(55)	1.835(27)
Ru(3)–C(06)	1.954(36)	Ru(5)–C(56)	1.885(26)
Ru(2)–C(07)	1.923(35)	Ru(5)–C(57)	1.950(33)
Ru(2)–C(8)	1.865	Ru(4)–C(58)	1.805(28)
Ru(2)–C(09)	1.888(33)	Ru(4)–C(59)	1.858(31)
Ru(2)–C(10)	1.822(33)	Ru(4)–C(60)	1.981(27)
C(01)–O(01)	1.192(28)	C(51)–O(51)	1.170
C(02)–O(02)	1.149(27)	C(52)–O(52)	1.135(35)
C(03)–O(03)	1.210(36)	C(53)–O(53)	1.127(31)
C(04)–O(04)	1.135(25)	C(54)–O(54)	1.209(33)
C(05)–O(05)	1.169(28)	C(55)–O(55)	1.156(27)
C(06)–O(06)	1.163(34)	C(56)–O(56)	1.134(28)
C(07)–O(07)	1.208(33)	C(57)–O(57)	1.205(32)
C(8)–O(8)	1.170	C(58)–O(58)	1.191(27)
C(09)–O(09)	1.146(33)	C(59)–O(59)	1.193(31)
C(10)–O(10)	1.202(32)	C(60)–O(60)	1.108(27)

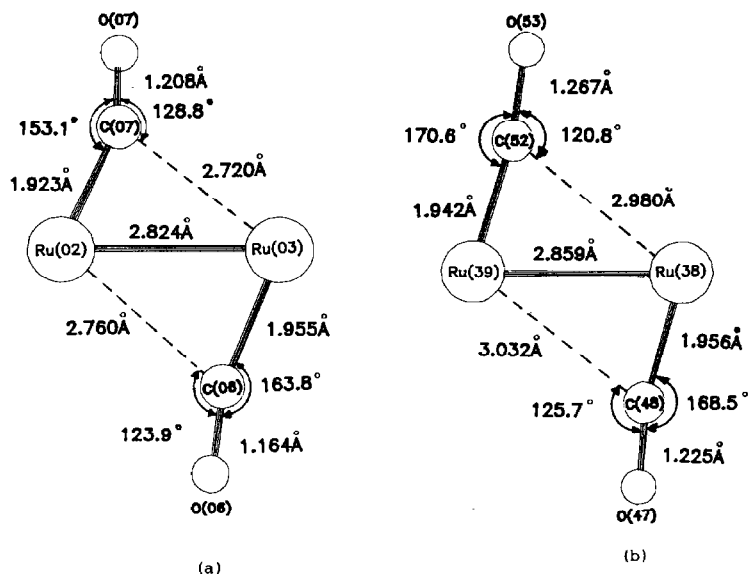


Fig. 4. Semibridging carbonyls along selected Ru-Ru bonds of (a) $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$ (molecule A), Ru(2) is $\text{Ru}(\text{CO})_4$ unit (this work); (b) $\text{Ru}_3(\text{CO})_{10}(\text{P}(\text{OCH}_3)_3)_2$; Ru(39) is $\text{Ru}(\text{CO})_4$ unit (calculated from positional data in ref. 10b).

above observations do not discount the possible contributions of the packing influence in promoting semibridging carbonyl ligands or twisting of the $\text{Ru}(\text{CO})_4$ unit [12].

The structure of several other phosphine and phosphite substituted triruthenium clusters have been reported [10]. Of particular interest is the comparison of the structures of $\text{Ru}_3(\text{CO})_{11}(\text{PPh}_3)$ and $\text{Ru}_3(\text{CO})_{10}(\text{P}(\text{OCH}_3)_3)_2$ to the bis(triphenylphosphine) derivative described here. For the monosubstituted derivative [10c], none of the Ru-C-O bond angles are less than 170° nor is there any other indication from the structure of semibridging behavior for the carbonyls. For $\text{Ru}_3(\text{CO})_{10}(\text{P}(\text{OCH}_3)_3)_2$, we have used published positional parameters to calculate Ru-C-O bond angles and Ru-C internuclear distances. This structure again shows twisting of the $\text{Ru}(\text{CO})_4$ group from the orientation found in $\text{Ru}_3(\text{CO})_{12}$ with CO semibridging between the $\text{Ru}(\text{CO})_4$ and $\text{Ru}(\text{CO})_3(\text{P}(\text{OCH}_3)_3)$ units (Fig. 3), however, this is less pronounced than in molecule A of $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$. The semibridging character of the carbonyls is similarly less pronounced as illustrated in Fig. 4b. Given that $\text{P}(\text{OCH}_3)_3$ is both less sterically demanding and less electron donating than PPh_3 , one cannot clearly separate the steric and electronic effects in this case either; indeed both are likely contributors.

The general features of the structure of $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$ are similar in both molecules A and B, including the observation of the twist of the $\text{Ru}(\text{CO})_4$ unit and corresponding CO semibridging. However, there are a few exceptions. In molecule B, one of "equatorial" carbonyls (52) is considerably more bent ($171(3)^\circ$) than its analogue (carbonyl (10)) in molecule A ($179(3)^\circ$). On the other hand, carbonyl (59) of molecule B is significantly less bent ($176(3)^\circ$) than its analogue (carbonyl (06)) in molecule A ($164(3)^\circ$). We have no obvious explanation for these differences other than to speculate that the potential surfaces governing the geometries of these carbonyl metal interactions are rather soft with respect to the bond angles.

In summary, we have shown that, for the $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$ cluster (and to a lesser extent for $\text{Ru}_3(\text{CO})_{10}(\text{P}(\text{OCH}_3)_3)_2$), the carbonyls of the $\text{Ru}(\text{CO})_4$ unit appear to rotate substantially from the orientation typical of the $\text{Ru}(\text{CO})_4$ unit of the $\text{Ru}_3(\text{CO})_{12}$ parent cluster. Such twisting of this group may in part be the result of avoidance of unfavorable steric interactions with the bulky triphenylphosphines on the adjacent ruthenium atoms. However, it is notable that such twisting also orients the two "axial" CO's for semibridging along two different Ru–Ru bonds. That compensating semibridging from carbonyls on the $\text{Ru}(\text{CO})_3(\text{PPh}_3)$ unit is less pronounced is consistent with Cotton's explanation [9] of the nature of semibridging interactions along bonds between non-equivalent metal centers.

Supplementary material available

Tables of thermal parameters (2 pages), hydrogen positions (1 page) and complete bond lengths and angles for $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$ (4 pages); listings of structure factors for $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$ (21 pages). These have been deposited under NAPS 04573, ASIS/NAPS, c/o Microfiche Publications P.O. Box 3513, Grand Central Station, New York, New York 10163–3515.

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(b) All least-squares refinements computed the agreement factors R and R_w according to:

$$R = \frac{\sum \|F_o\| - \|F_c\|}{\sum \|F_o\|}$$

$$R_w = \text{sqrt} \left[\frac{\sum w \|F_o\| - \|F_c\|^2}{\sum w \|F_o\|^2} \right]$$

where: F_o is the observed structure factor, F_c is the calculated structure factor, and $w = 1/F_o^2$.

(c) Scattering factors and correction for anomalous dispersion were taken from "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

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