Journal of Organometallic Chemistry, 395 (1990) 85–103
Elsevier Sequoia S.A., Lausanne
JOM 21048

Crystal structure of $[Ph_3PCH_2CH_2PPh_3^{2+}]$-$[Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}] \cdot 2Me_2CO$ and some brief comments on the severely disordered structure of $[NEt_4^+]_2[Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}]$

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(Received February 19th, 1990)

Abstract

The species $[Ph_3PCH_2CH_2PPh_3^{2+}][Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}] \cdot 2Me_2CO$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (No. 2) with a 12.8846(25), b 15.3253(26), c 20.4478(41) Å, α 104.494(15)°, β 96.514(16)°, γ 94.674(15)°, V 3858.5(13) Å^3 and $Z = 2$. Diffraction data (Mo-K_α, $2\theta = 4.5$–$40.0°$) were collected on a Syntex $P2_1$ diffractometer and the structure was refined to R 4.6% for those 6381 independent reflections with $|F_o| > 1.0\sigma(|F_o|)$. The decanuclear dianion is based upon an edge-bridged bisoctahedron (with each octahedral fragment containing a μ_6-C atom) and has approximate D_2 symmetry. Each ruthenium atom is associated with two terminal carbonyl ligands; in addition, all but the edge-fused ruthenium atoms are linked pair-wise by single, symmetrically bridging carbonyl ligands. The species $[NEt_4^+]_2[Ru_{10}(\mu_6\text{-}C)(CO)_{20}(\mu\text{-}CO)_4^{2-}]$ has also been studied. The Ru_{10} cluster lies on a site of $\bar{1}$ symmetry (space group $P2_1/c$, $Z = 2$) and the resulting disorder led to only a partial solution to this structure.

Introduction

Treatment of $Os_3(CO)_{12}$ with sodium in diglyme at 162°C yields $Os_6(CO)_{18}^{2-}$. Pyrolysis of this product (triglyme, 216°C) yields $Os_{10}C(CO)_{24}^{2-}$ [1], a "134-electron" cluster. This species has been shown to possess a tetracapped octahedral array of osmium atoms [2]. Treatment of $Ru_3(CO)_{12}$ with sodium (THF, 66°C) yields $Ru_6(CO)_{18}^{2-}$, but pyrolysis of this proceeds by a route different from that of the osmium analogue. Thus, $Ru_6(CO)_{18}^{2-}$ is converted to $Ru_6C(CO)_{16}^{2-}$ (+CO_2) in refluxing diglyme at 162 ° C [1]. Pyrolysis of this product (tetraglyme, 210–230 ° C, 80 h) produces the dicarbido species $Ru_{10}C_2(CO)_{24}^{2-}$ [3], a "138-electron" cluster.

We now report the solution of the crystal structure of the $[Ph_3PCH_2CH_2PPh_3^{2+}]$ salt of $Ru_{10}C_2(CO)_{24}^{2-}$ along with a partial solution of the disordered structure of the $[NEt_4^+]$ salt of this dianion.

Collection of X-ray diffraction data for $[Ph_3PCH_2CH_2PPh_3^{2+}][Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}] \cdot 2Me_2CO$

The crystal used for the X-ray diffraction study was a purple plate of dimensions 0.06 × 0.18 × 0.25 mm. It was sealed into a thin-walled glass capillary, mounted on a eucentric goniometer and aligned on the Syntex $P2_1$ four-circle diffractometer at SUNY-Buffalo. Crystal alignment, determination of Laue group ($\bar{1}$, triclinic), orientation matrix and cell dimensions were all carried out as described previously [4]; details appear in Table 1. All data were corrected for Lorentz and polarization factors and for the effects of absorption. Data were placed on an approximately absolute scale by means of a Wilson plot. Possible space groups are $P1$ (C_1^1; No. 1) or $P\bar{1}$ (C_i^1; No. 2). The latter, centrosymmetric, possibility was strongly indicated by intensity statistics and unit cell volume (consistent with $Z = 2$) and was confirmed by the successful solution of the structure in this higher symmetry space group.

Table 1

Experimental data for the X-ray diffraction study of $[Ph_3PCH_2CH_2PPh_3^{2+}][Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}] \cdot 2Me_2CO$

(A) Unit Cell Data

$a = 12.8846(25)$ Å

$b = 15.3253(26)$ Å

$c = 20.4478(41)$ Å

$\alpha = 104.494(15)°$

$\beta = 96.514(16)°$

$\gamma = 94.674(15)°$

$V = 3858.5(13)$ Å^3

$\mu = 19.71$ cm^{-1}

crystal system: triclinic

space group: $P\bar{1}$ (No. 2)

$Z = 2$

formula: $C_{70}H_{46}O_{26}P_2Ru_{10}$

molec. wt = 2375.8

D(calc'd) = 2.045 g cm^{-3}

$T = 24$ ° C (297 K)

$F(000) = 2288$

(B) Collection of X-ray diffraction data

Diffractometer: Syntex $P2_1$

Radiation: Mo-K_α ($\lambda = 0.710730$Å)

Monochromator: highly oriented (pyrolytic) graphite; equatorial mode with $2\theta(\text{mono}) = 12.160°$; assumed to be 50% perfect/50% ideally mosaic for polarization correction

Reflections measured: $+h$, $\pm k$, $\pm l$ for $2\theta = 4.5–40.0°$. A total of 7881 reflections were collected and merged ($R_{Av} = 3.7\%$) to 6381 reflections with $|F_o| > 1.0\sigma(|F_o|)$.

Scan conditions: coupled θ(crystal)–2θ(counter) scan at 3.5 deg/min in 2θ, from $[2\theta(K_{\alpha1}) - 1.0]°$ to $[2\theta(K_{\alpha2}) + 1.0]°$

Backgrounds: stationary-crystal, stationary-counter at the two extremes of the 2θ scan; each for one-quarter of the total scan time.

Standard reflections: three approximately mutually orthogonal reflections were collected before each batch of 97 data. No significant fluctuations nor decay were observed.

Absorption correction: data were corrected empirically by interpolation (in 2θ and ϕ) between the normalized transmission curves of a series of close-to-axial (ψ-scan) reflections.

Because of the large number of atoms and variables (which could not be accommodated by the $P2_1$/XTL system at SUNY-Buffalo), refinement was carried out on the Nicolet R3 system at the University of Delaware; the SHELXTL programs (Revision 3.0) were used. The structure was solved by direct methods and refinement converged with $R_F = 4.6\%$, $R_{wF} = 5.2\%$ and GOF = 1.02 for those 6381 independent reflections with $|F_o| > 1.0\sigma(|F_o|)$. All 108 nonhydrogen atoms were refined with anisotropic thermal parameters and all hydrogen atoms were included in optimized positions with $d(\text{C–H}) = 0.96$ Å [5]. The structure thus included 154 atoms and 974 variables. Despite the rather low data-to-parameter ratio of 6.55 : 1, the structural refinement was well-behaved, symmetry-equivalent distances are in excellent agreement (vide infra) and the resulting thermal vibration ellipsoids are inherently sensible.

A final difference-Fourier map showed features only in the range −1.42 to +0.98 e⁻; the structure is thus both correct and complete.

Final atomic coordinates and anisotropic thermal parameters appear as Tables 2 and 3.

Description of the structure of $[Ph_3PCH_2CH_2PPh_3^{2+}][Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}]$ · $2Me_2CO$

The crystal consists of discrete ordered units of $[Ph_3PCH_2CH_2PPh_3^{2+}]$ cations, $[Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}]$ anions and acetone of crystallization in a 1 : 1 : 2 ratio. The presence of acetone was originally unsuspected; the geometry of these fragments is, however, definitive, particularly when associated with the crystallization of this salt from this particular solvent. A stereoscopic view of the unit cell appears as Fig. 1 and an atomic numbering diagram for the cation appears as Fig. 2.

Interatomic distances and angles are collected in Tables 4 and 5.

The $[Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}]$ anion

The labelling of atoms in this anion is shown in Figs. 3 and 4. This anion is formed by pyrolysis of $[Ru_6(\mu_6\text{-}C)(CO)_{16}^{2-}]$, vide supra, and can be related to that species.

The $[Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}]$ anion contains a ten-atom metallic framework (of a type unique among metal carbonyl clusters) based upon two octahedral $Ru_6(\mu_6\text{-}C)$ moieties fused along a common equatorial edge (i.e., Ru(9)-Ru(10)). [Alternatively, the cluster core can be viewed as two square-pyramidal Ru_5C units attached, off axis, at their square bases. In this description, atoms Ru(2) and Ru(6) are the apical atoms of the two Ru_5C units—see Fig. 4.] The ten ruthenium atoms define a portion of a body-centered-cubic array. Each ruthenium atom is associated with two terminal carbonyl ligands. In addition, all but the edge-fused ruthenium atoms (Ru(9) and Ru(10)) are linked pairwise by single, symmetrically bridging carbonyl ligands which span the apical-equatorial ruthenium-ruthenium bonds. The two μ_6-carbide ligands lie essentially in the principal equatorial plane. The entire anion has approximate (non-crystallographic) D_2 symmetry (see Fig. 5). The dianions are thus chiral, but the crystal contains an ordered racemic mixture of the two enantiomers, which are interrelated by crystallographic inversion centers. Stereoscopic views of this anion are provided in Fig. 6.

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Table 2

Atomic coordinates ($\times 10^4$) and thermal parameters ($\times 10^3$) for $[Ph_3PCH_2CH_2PPh_3^{2+}][Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}]\cdot 2Me_2CO$

Atom	x	y	z	U(Å^2) [a]
(A) Atoms in the $[Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}]$ *anion*				
Ru(1)	7611(1)	1496(1)	7902(1)	37
Ru(2)	8272(1)	3125(1)	9078(1)	38
Ru(3)	9212(1)	1420(1)	8939(1)	40
Ru(4)	10399(1)	3140(1)	8871(1)	38
Ru(5)	11160(1)	2962(1)	7453(1)	40
Ru(6)	10302(1)	1565(1)	6300(1)	44
Ru(7)	9496(1)	3344(1)	6462(1)	45
Ru(8)	8091(1)	1869(1)	6520(1)	41
Ru(9)	8890(1)	3219(1)	7762(1)	34
Ru(10)	9738(1)	1515(1)	7620(1)	35
O(1a)	6310(7)	−122(6)	6905(5)	78
O(1b)	5603(7)	2163(6)	8353(5)	75
O(2a)	7130(6)	2805(5)	10218(4)	86
O(2b)	7178(10)	4811(7)	9196(6)	111
O(3a)	10397(8)	−198(7)	8929(7)	112
O(3b)	8931(9)	1581(7)	10401(5)	101
O(4a)	11964(8)	2349(7)	9695(5)	92
O(4b)	11941(8)	4834(6)	9169(5)	86
O(5a)	13241(7)	2965(7)	8313(5)	89
O(5b)	11979(8)	4786(6)	7316(6)	90
O(6a)	11106(8)	−236(6)	6268(6)	89
O(6b)	10426(10)	1361(8)	4804(5)	101
O(7a)	10630(11)	3514(8)	5276(6)	118
O(7b)	8831(9)	5226(6)	6625(5)	94
O(8a)	5723(8)	1809(7)	6273(6)	96
O(8b)	7859(8)	152(6)	5390(5)	85
O(9a)	6742(7)	3826(6)	7502(5)	81
O(9b)	9869(7)	5173(5)	8219(4)	58
O(10a)	8901(7)	−450(5)	6999(5)	79
O(10b)	11811(7)	916(6)	8082(5)	67
Obr(1)	7280(5)	75(4)	8674(3)	65
Obr(2)	9912(7)	4113(6)	10250(4)	73
Obr(3)	12540(7)	2317(5)	6379(4)	61
Obr(4)	7620(8)	2759(7)	5379(5)	80
C(1a)	6809(9)	524(8)	7262(6)	50
C(1b)	6393(9)	1936(8)	8196(7)	56
C(2a)	7569(10)	2908(9)	9784(7)	55
C(2b)	7614(11)	4164(8)	9156(7)	63
C(3a)	9936(10)	418(8)	8932(7)	67
C(3b)	9024(11)	1545(9)	9839(7)	65
C(4a)	11335(7)	2621(7)	9378(5)	62
C(4b)	11372(10)	4191(8)	9051(6)	58
C(5a)	12448(9)	2982(8)	8007(6)	57
C(5b)	11624(8)	4084(6)	7332(5)	60
C(6a)	10777(10)	440(8)	6243(7)	61
C(6b)	10359(8)	1438(6)	5374(5)	68
C(7a)	10198(13)	3443(11)	5732(8)	70
C(7b)	9095(11)	4513(9)	6559(7)	68
C(8a)	6615(7)	1794(7)	6393(5)	58
C(8b)	8016(10)	799(8)	5817(6)	61

Table 2 (continued)

Atom	x	y	z	$U(\text{Å}^2)$ [a]
C(9a)	7258(10)	3548(8)	7587(6)	52
C(9b)	9545(9)	4422(7)	8048(5)	48
C(10a)	9145(7)	316(5)	7208(5)	56
C(10b)	11036(9)	1184(7)	7916(6)	52
Cbr(1)	7802(9)	682(8)	8574(6)	51
Cbr(2)	7658(9)	3705(7)	9686(6)	47
Cbr(3)	11742(10)	2274(7)	6604(6)	43
Cbr(4)	8128(11)	2692(9)	5878(7)	58
Cc(1)	9012(8)	2322(7)	8367(5)	30
Cc(2)	9606(9)	2415(7)	7016(5)	38
(B) Atoms in the $[Ph_3PCH_2CH_2PPh_3^{2+}]$ *cation*				
P(1)	6325(2)	1078(2)	2080(2)	42
P(2)	4246(3)	3157(2)	2937(2)	46
C(11)	6384(9)	521(7)	2761(5)	43
C(12)	6165(9)	−405(8)	2606(6)	48
C(13)	6144(10)	−801(9)	3140(7)	61
C(14)	6332(10)	−283(9)	3794(6)	73
C(15)	6583(8)	644(7)	3958(5)	68
C(16)	6613(9)	1044(8)	3426(6)	59
C(21)	7515(7)	1824(6)	2166(5)	46
C(22)	8413(9)	1651(8)	2525(6)	58
C(23)	9363(12)	2194(9)	2527(7)	77
C(24)	9367(11)	2905(8)	2229(6)	64
C(25)	8435(10)	3046(8)	1862(6)	66
C(26)	7519(10)	2489(7)	1820(5)	47
C(31)	6149(9)	272(7)	1275(5)	46
C(32)	5206(10)	−265(8)	1037(6)	64
C(33)	5067(11)	−911(8)	423(7)	71
C(34)	5891(10)	−996(7)	35(5)	86
C(35)	6824(12)	−463(10)	265(7)	71
C(36)	6973(8)	173(7)	878(5)	56
C(41)	4658(9)	4326(7)	3275(5)	48
C(42)	5368(9)	4798(6)	2990(6)	85
C(43)	5671(2)	5721(10)	3272(7)	98
C(44)	5253(9)	6182(6)	3810(6)	85
C(45)	4524(13)	5734(11)	4060(8)	109
C(46)	4243(11)	4831(10)	3822(7)	92
C(51)	3191(8)	2980(6)	2263(5)	45
C(53)	2902(11)	3687(9)	1990(6)	70
C(53)	2053(10)	3529(9)	1467(6)	82
C(54)	1505(12)	2676(10)	1226(7)	84
C(55)	1833(11)	1972(10)	1474(7)	81
C(56)	2645(9)	2142(7)	1990(5)	63
C(61)	3796(10)	2675(8)	3580(6)	57
C(62)	4495(11)	2411(8)	4025(6)	77
C(63)	4112(13)	2064(9)	4551(7)	98
C(64)	3057(13)	2056(9)	4588(7)	98
C(65)	2372(14)	2351(10)	4174(8)	105
C(66)	2736(12)	2639(9)	3675(7)	83
C(71)	5166(7)	1702(6)	2136(4)	42
C(72)	5374(8)	2636(6)	2632(5)	47
H(12)	6051	−754	2138	62
H(13)	5994	−1448	3050	80
H(14)	6243	−574	4152	85

(continued)

Table 2 (continued)

Atom	x	y	z	$U(\AA^2)$ [a]
H(15)	6730	1001	4423	85
H(16)	6853	1676	3505	62
H(22)	8419	1166	2744	81
H(23)	10013	2112	2772	93
H(24)	10011	3280	2251	85
H(25)	8454	3536	1647	70
H(26)	6893	2580	1554	65
H(32)	4637	−179	1303	73
H(33)	4408	−1285	259	77
H(34)	5800	−1433	−401	83
H(35)	7396	−514	−0	98
H(36)	7635	538	1054	65
H(42)	5652	4450	2606	86
H(43)	6198	6019	3080	97
H(44)	5422	6827	3985	90
H(45)	4216	6083	4433	113
H(46)	3762	4537	4047	98
H(52)	3244	4286	2211	88
H(53)	1886	4003	1256	97
H(54)	907	2551	876	108
H(55)	1454	1378	1292	96
H(56)	2834	1647	2172	77
H(62)	5231	2484	3989	88
H(63)	4558	1844	4868	115
H(64)	2778	1811	4929	102
H(65)	1647	2346	4243	126
H(66)	2261	2840	3360	99
H(71a)	4626	1363	2288	45
H(71b)	4923	1758	1688	45
H(72a)	5848	2596	3019	54
H(72b)	5710	3028	2400	54
(C) Atoms in acetone, Molecule 1				
Ao(1)	5155(7)	3233(6)	1200(5)	97
Ac(1)	4504(11)	3519(9)	180(6)	101
Ah(1a)	4554	4059	22	108
Ah(1b)	3777	3317	175	108
Ah(1c)	4818	3054	−114	108
Ac(2)	5080(10)	3760(9)	862(7)	75
Ac(3)	5552(10)	4711(8)	1131(6)	114
Ah(3a)	5417	5047	798	108
Ah(3b)	6297	4722	1247	108
Ah(3c)	5253	4981	1533	108
(D) Atoms in acetone, Molecule 2				
Ao(2)	6881(7)	3451(5)	3987(4)	135
Ac(4)	8653(11)	3968(9)	4072(7)	140
Ah(4a)	9096	4510	4323	108
Ah(4b)	8651	3897	3592	108
Ah(4c)	8915	3454	4195	108
Ac(5)	7591(12)	3994(10)	4232(7)	86
Ac(6)	7419(10)	4815(8)	4742(6)	129
Ah(6a)	8056	5223	4887	108
Ah(6b)	7204	4627	5125	108
Ah(6c)	6877	5117	4559	108

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[a] For all non-hydrogen atoms, U values are equivalent isotropic values, defined as one-third of the trace of the orthogonalized 3×3 U_{ij} tensor.

Table 3

Anisotropic thermal parameters [a] ($\text{Å}^2 \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	27(1)	34(1)	55(1)	16(1)	9(1)	6(1)
Ru(2)	33(1)	36(1)	51(1)	14(1)	17(1)	11(1)
Ru(3)	33(1)	38(1)	56(1)	23(1)	11(1)	10(1)
Ru(4)	29(1)	39(1)	47(1)	9(1)	10(1)	6(1)
Ru(5)	30(1)	38(1)	51(1)	8(1)	14(1)	4(1)
Ru(6)	39(1)	44(1)	49(1)	5(1)	16(1)	7(1)
Ru(7)	46(1)	43(1)	52(1)	20(1)	13(1)	5(1)
Ru(8)	34(1)	42(1)	50(1)	16(1)	5(1)	4(1)
Ru(9)	30(1)	30(1)	46(1)	14(1)	11(1)	8(1)
Ru(10)	29(1)	30(1)	48(1)	11(1)	11(1)	9(1)
O(1a)	47(6)	75(7)	99(7)	6(6)	0(6)	−9(5)
O(1b)	35(6)	74(7)	115(8)	16(6)	22(6)	16(5)
O(2a)	80(6)	118(6)	79(5)	40(5)	45(4)	24(5)
O(2b)	136(11)	92(8)	136(10)	47(7)	68(9)	74(8)
O(3a)	76(8)	94(8)	206(12)	91(8)	44(8)	42(7)
O(3b)	130(10)	112(8)	78(7)	44(6)	25(7)	39(8)
O(4a)	72(7)	108(8)	97(8)	34(7)	−7(6)	25(6)
O(4b)	70(7)	74(7)	103(8)	−2(6)	36(6)	−6(6)
O(5a)	43(6)	114(8)	101(8)	18(6)	−5(6)	7(6)
O(5b)	72(7)	55(6)	152(10)	34(6)	38(7)	3(5)
O(6a)	59(7)	72(6)	134(9)	17(6)	16(6)	21(5)
O(6b)	130(1)	114(9)	52(6)	8(6)	32(7)	−14(8)
O(7a)	159(12)	117(9)	107(9)	54(7)	81(8)	15(8)
O(7b)	115(9)	69(7)	106(8)	34(6)	14(7)	26(6)
O(8a)	45(7)	109(8)	156(10)	79(8)	3(7)	4(6)
O(8b)	109(8)	63(6)	66(6)	−9(5)	−1(6)	10(6)
O(9a)	47(6)	90(7)	113(8)	34(6)	11(6)	33(5)
O(9b)	62(6)	35(5)	75(6)	6(4)	22(5)	4(4)
O(10a)	72(7)	44(5)	114(8)	4(5)	30(6)	1(5)
O(10b)	45(6)	79(6)	92(7)	39(5)	23(5)	28(5)
Obr(1)	57(4)	61(4)	92(5)	45(4)	24(4)	3(3)
Obr(2)	57(6)	87(7)	64(6)	−5(5)	20(5)	4(5)
Obr(3)	51(6)	56(5)	79(6)	15(6)	33(5)	−2(5)
Obr(4)	83(8)	90(8)	74(7)	44(6)	−5(6)	3(6)
C(1a)	26(7)	53(8)	71(9)	14(7)	4(6)	11(6)
C(1b)	35(8)	47(8)	85(10)	11(7)	16(7)	13(6)
C(2a)	44(8)	77(9)	61(9)	35(7)	24(7)	23(7)
C(2b)	61(10)	61(8)	74(10)	24(7)	21(8)	21(7)
C(3a)	47(8)	61(8)	113(11)	50(8)	21(8)	18(7)
C(3b)	84(10)	62(9)	56(9)	24(7)	11(8)	14(8)
C(4a)	45(6)	84(7)	65(6)	27(5)	10(5)	24(5)
C(4b)	47(8)	58(8)	60(8)	−4(6)	30(7)	−14(7)
C(5a)	43(8)	55(8)	65(8)	−1(6)	18(7)	−7(6)
C(5b)	49(6)	58(6)	78(7)	17(5)	27(5)	10(5)
C(6a)	41(8)	49(7)	95(10)	17(7)	15(7)	16(6)
C(6b)	76(8)	62(6)	59(7)	4(5)	13(6)	0(6)
C(7a)	88(12)	71(11)	66(11)	39(9)	26(10)	7(10)
C(7b)	70(10)	70(9)	77(10)	37(8)	17(8)	16(8)
C(8a)	38(6)	61(6)	74(7)	27(5)	−10(5)	−10(5)
C(8b)	69(9)	50(8)	59(8)	13(6)	−1(7)	6(7)
C(9a)	33(8)	65(7)	69(8)	30(6)	9(7)	20(6)
C(9b)	41(8)	44(7)	66(7)	21(6)	20(6)	5(6)
C(10a)	50(6)	36(5)	81(7)	10(5)	14(5)	3(4)
C(10b)	44(8)	52(7)	69(8)	19(6)	24(6)	22(6)
Cbr(1)	43(7)	57(8)	65(9)	27(7)	27(7)	23(6)

(continued)

Table 3 (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cbr(2)	44(8)	44(7)	47(7)	3(6)	11(6)	1(6)
Cbr(3)	45(8)	42(7)	53(8)	24(6)	19(7)	8(6)
Cbr(4)	65(10)	51(9)	65(9)	25(7)	11(8)	19(7)
Cc(1)	24(7)	36(7)	41(7)	17(6)	20(6)	18(5)
Cc(2)	32(8)	38(7)	54(8)	24(6)	13(6)	3(6)
P(1)	34(2)	39(2)	57(2)	17(1)	13(1)	9(1)
P(2)	45(2)	35(2)	61(2)	12(1)	23(2)	11(1)
C(11)	22(7)	52(7)	64(8)	24(6)	16(6)	12(6)
C(12)	27(8)	54(8)	68(8)	24(6)	9(6)	11(6)
C(13)	55(10)	60(9)	79(10)	37(8)	10(8)	13(7)
C(14)	47(8)	115(10)	84(9)	76(8)	11(7)	14(7)
C(15)	64(7)	82(7)	64(7)	30(6)	−0(6)	23(6)
C(16)	54(8)	63(7)	62(8)	21(7)	5(6)	12(6)
C(21)	28(5)	46(6)	63(6)	6(5)	19(5)	1(4)
C(22)	40(7)	54(8)	74(9)	10(7)	−2(6)	2(6)
C(23)	35(11)	100(10)	93(10)	23(8)	9(8)	1(9)
C(24)	53(10)	58(9)	89(9)	17(7)	39(8)	5(8)
C(25)	72(9)	44(8)	85(8)	17(6)	23(7)	0(7)
C(26)	41(8)	45(7)	64(7)	24(6)	29(6)	3(7)
C(31)	45(7)	40(6)	54(6)	13(5)	12(6)	4(6)
C(32)	76(10)	45(8)	65(9)	4(7)	13(7)	14(7)
C(33)	70(10)	48(9)	84(9)	14(7)	−15(8)	−8(7)
C(34)	135(10)	52(6)	72(7)	14(5)	10(7)	16(6)
C(35)	80(12)	65(10)	71(11)	13(9)	23(9)	22(9)
C(36)	57(7)	58(7)	57(7)	14(5)	20(6)	25(5)
C(41)	47(7)	38(6)	58(7)	1(6)	23(6)	9(6)
C(42)	96(8)	49(6)	113(9)	11(6)	54(7)	5(6)
C(43)	90(11)	75(10)	128(10)	20(8)	23(9)	5(8)
C(44)	92(9)	37(5)	112(9)	−6(6)	16(7)	1(5)
C(45)	144(12)	60(13)	114(11)	−12(10)	58(10)	19(10)
C(46)	110(11)	52(11)	114(10)	6(8)	54(9)	5(9)
C(51)	39(7)	39(6)	58(6)	6(5)	20(5)	19(5)
C(52)	64(10)	68(9)	81(9)	19(7)	22(8)	23(8)
C(53)	63(9)	115(10)	94(9)	59(8)	26(8)	30(8)
C(54)	46(11)	113(11)	90(11)	28(9)	1(9)	5(9)
C(55)	71(10)	72(10)	97(9)	16(8)	21(8)	−1(8)
C(56)	50(8)	61(7)	76(7)	17(6)	10(6)	4(6)
C(61)	71(9)	44(8)	61(8)	8(6)	31(7)	12(7)
C(62)	96(9)	77(8)	67(9)	20(7)	27(8)	33(7)
C(63)	159(13)	77(11)	62(11)	14(9)	22(10)	39(9)
C(64)	127(12)	99(10)	81(10)	39(8)	49(9)	−18(8)
C(65)	96(13)	142(12)	84(12)	33(10)	49(11)	−12(10)
C(66)	77(11)	109(9)	72(10)	27(8)	48(8)	−1(8)
C(71)	46(6)	33(5)	49(5)	8(4)	15(5)	13(5)
C(72)	37(7)	50(6)	56(6)	13(5)	14(5)	11(5)
Ao(1)	97(7)	115(7)	110(7)	65(6)	37(5)	39(6)
Ac(1)	120(10)	80(9)	97(10)	23(8)	−8(8)	8(8)
Ac(2)	63(10)	80(9)	94(10)	38(8)	25(8)	16(7)
Ac(3)	89(10)	127(10)	128(9)	57(8)	−8(8)	−23(8)
Ao(2)	142(7)	101(6)	139(7)	38(5)	−53(6)	−39(5)
Ac(4)	151(11)	134(9)	137(9)	27(7)	35(8)	28(8)
Ac(5)	95(11)	84(10)	76(9)	23(8)	8(8)	−7(8)
Ac(6)	134(10)	117(9)	136(9)	28(8)	42(8)	−7(8)

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[a] The anisotropic thermal parameters enter the natural exponent for F_c in the form: $-2\pi^2(h^2a^{*2}U_{11}+\ldots+2hka^*b^*U_{12}+\ldots)$

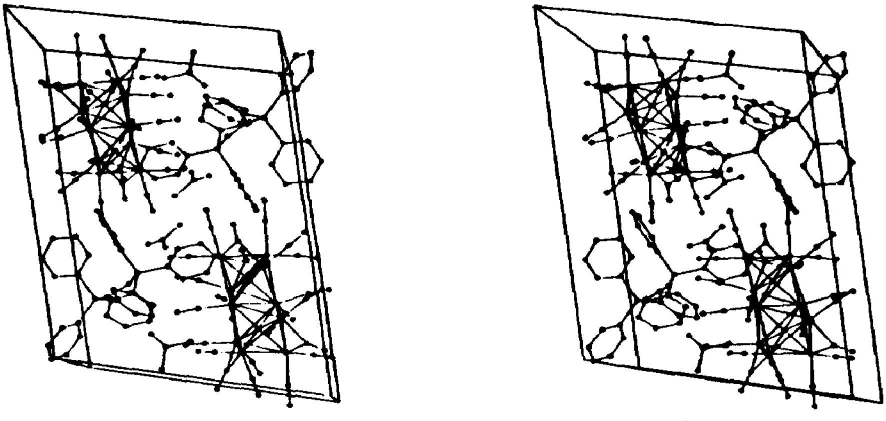

Fig. 1. Stereoscopic view of the unit cell for $[Ph_3PCH_2CH_2PPh_3^{2+}][Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}]\cdot 2Me_2CO$ (*c* vertical, *b* horizontal, *a* into page).

The individual Ru–Ru bond lengths range from 2.803 (1) to 3.098(2) Å. [For reasons discussed below, we regard the vectors Ru(1) ··· Ru(8) = 3.138(2) Å and Ru(4) ··· Ru(5) = 3.122(2) Å as non-bonding.] These intermetallic distances do, however, fall into distinct sets based upon the D_2 symmetry of the anion. The shortest are those Ru(axial)–Ru(equatorial) bonds that are bridged by carbonyl ligands [Ru(1)–Ru(3) = 2.816(1), Ru(2)–Ru(4) = 2.819(2), Ru(5)–Ru(6) = 2.802(1), Ru(7)–Ru(8) = 2.814(2) Å; average = 2.813 Å], while the longest are alternate Ru(apical)–Ru(fused) bonds [Ru(1)–Ru(9) = 3.089(1), Ru(4)–Ru(10) = 3.072(1), Ru(5)–Ru(9) = 3.098(2), Ru(8)–Ru(10) = 3.094(2) Å; average = 3.088 Å]. The intermediate Ru–Ru distances also separate cleanly into groups based upon the D_2 symmetry of the anion. In order of increasing Ru–Ru distance, we have the following sets.

(continued on p. 100)

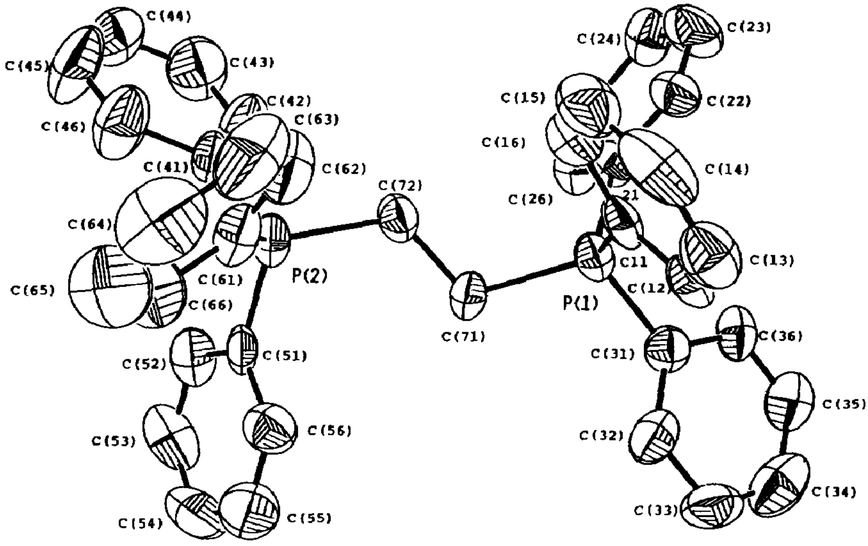

Fig. 2. Numbering of atoms in the $Ph_3PCH_2CH_2PPh_3^{2+}$ cation.

Table 4

Interatomic distances (Å) in $[Ph_3PCH_2CH_2PPh_3^{2+}][Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}]\cdot 2Me_2CO$

(A) Ru–Ru distances			
Ru(1)–Ru(2)	2.986(1)	Ru(5)–Ru(6)	2.803(1)
Ru(1)–Ru(3)	2.816(1)	Ru(5)–Ru(7)	2.976(2)
Ru(1) ··· Ru(8)	3.138(2)	Ru(5)–Ru(9)	3.098(2)
Ru(1)–Ru(9)	3.089(1)	Ru(5)–Ru(10)	2.873(1)
Ru(1)–Ru(10)	2.863(1)	Ru(6)–Ru(7)	2.950(2)
Ru(2)–Ru(3)	2.931(2)	Ru(6)–Ru(8)	2.990(2)
Ru(2)–Ru(4)	2.819(2)	Ru(6)–Ru(10)	2.892(2)
Ru(2)–Ru(9)	2.925(2)	Ru(7)–Ru(8)	2.814(2)
Ru(3)–Ru(4)	2.979(2)	Ru(7)–Ru(9)	2.901(2)
Ru(3)–Ru(10)	2.889(2)	Ru(8)–Ru(9)	2.866(1)
Ru(4) ··· Ru(5)	3.122(2)	Ru(8)–Ru(10)	3.094(2)
Ru(4)–Ru(9)	2.849(1)	Ru(9)–Ru(10)	2.872(1)
Ru(4)–Ru(10)	3.072(1)		
(B) Ru–CO (terminal) distances			
Ru(1)–C(1a)	1.862(10)	Ru(6)–C(6a)	1.857(13)
Ru(1)–C(1b)	1.860(13)	Ru(6)–C(6b)	1.865(10)
Ru(2)–C(2a)	1.872(14)	Ru(7)–C(7a)	1.861(18)
Ru(2)–C(2b)	1.845(14)	Ru(7)–C(7b)	1.874(14)
Ru(3)–C(3a)	1.860(14)	Ru(8)–C(8a)	1.879(9)
Ru(3)–C(3b)	1.847(15)	Ru(8)–C(8b)	1.879(11)
Ru(4)–C(4a)	1.857(10)	Ru(9)–C(9a)	1.885(13)
Ru(4)–C(4b)	1.891(12)	Ru(9)–C(9b)	1.884(10)
Ru(5)–C(5a)	1.894(12)	Ru(10)–C(10a)	1.877(8)
Ru(5)–C(5b)	1.859(10)	Ru(10)–C(10b)	1.867(12)
(C) Ru–Co(bridging) distances			
Ru(1)–Cbr(1)	2.082(14)	Ru(5)–Cbr(3)	2.047(12)
Ru(3)–Cbr(1)	2.018(11)	Ru(6)–Cbr(3)	2.020(11)
Ru(2)–Cbr(2)	2.052(11)	Ru(7)–Cbr(4)	2.042(12)
Ru(4)–Cbr(2)	2.053(12)	Ru(8)–Cbr(4)	2.036(15)
(D) Ru–(μ_6-C) distances			
Ru(1)–Cc(1)	2.098(9)	Ru(5)–Cc(2)	2.110(10)
Ru(2)–Cc(1)	2.037(10)	Ru(6)–Cc(2)	2.044(11)
Ru(3)–Cc(1)	2.035(12)	Ru(7)–Cc(2)	2.034(12)
Ru(4)–Cc(1)	2.096(9)	Ru(8)–Cc(2)	2.098(10)
Ru(9)–Cc(1)	2.071(12)	Ru(9)–Cc(2)	2.063(11)
Ru(10)–Cc(1)	2.074(10)	Ru(10)–Cc(2)	2.073(12)
(E) Terminal C–O distances			
C(1a)–O(1a)	1.163(13)	C(1b)–O(1b)	1.156(16)
C(2a)–O(2a)	1.141(16)	C(2b)–O(2b)	1.169(18)
C(3a)–O(3a)	1.154(18)	C(3b)–O(3b)	1.157(18)
C(4a)–O(4a)	1.149(15)	C(4b)–O(4b)	1.136(15)
C(5a)–O(5a)	1.142(15)	C(5b)–O(5b)	1.143(14)
C(6a)–O(6a)	1.161(16)	C(6b)–O(6b)	1.155(15)
C(7a)–O(7a)	1.161(22)	C(7b)–O(7b)	1.152(17)
C(8a)–O(8a)	1.152(14)	C(8b)–O(8b)	1.131(13)
C(9a)–O(9a)	1.143(16)	C(9b)–O(9b)	1.144(13)
C(10a)–O(10a)	1.147(11)	C(10b)–O(10b)	1.158(15)
(F) Bridging C–O distances			
Cbr(1)–Obr(1)	1.177(14)	Cbr(3)–Obr(3)	1.177(14)
Cbr(2)–Obr(2)	1.160(13)	Cbr(4)–Obr(4)	1.181(17)

Table 4 (continued)

(G) P–C distances within $Ph_3PCH_2CH_2PPh_3^{2+}$ cation			
P(1)–C(11)	1.804(13)	P(1)–C(21)	1.800(9)
P(1)–C(31)	1.772(9)	P(1)–C(71)	1.837(10)
P(2)–C(41)	1.763(10)	P(2)–C(51)	1.774(10)
P(2)–C(61)	1.790(14)	P(2)–C(72)	1.812(10)
(H) Distances within acetone molecules			
Ac(1)–Ac(2)	1.448(18)	Ac(4)–Ac(5)	1.443(21)
Ac(2)–Ac(3)	1.475(17)	Ac(5)–Ac(6)	1.470(18)
Ac(2)–Ao(1)	1.190(19)	Ac(5)–Ao(2)	1.160(16)

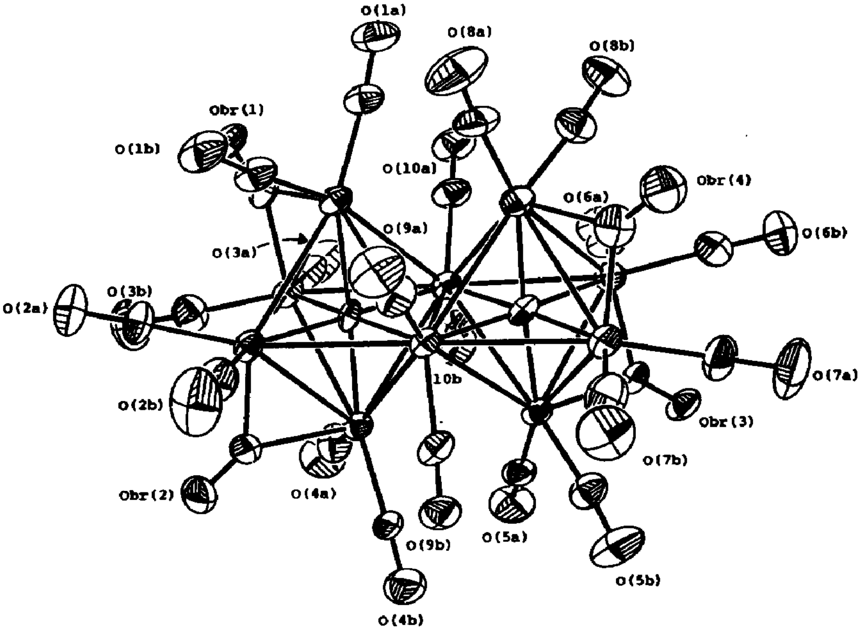

Fig. 3. Labelling of carbonyl ligands in the $Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}$ anion.

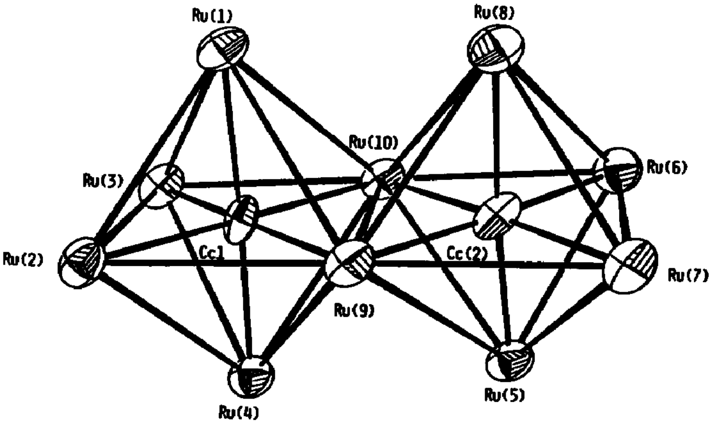

Fig. 4. The $Ru_{10}(\mu_6\text{-}C)_2$ core of the anion. (Same orientation as in Fig. 3.)

Table 5

Interatomic angles (°)

(A) Angles around ruthenium atoms			
Ru(2)–Ru(1)–Ru(3)	60.6	Ru(2)–Ru(1)–Ru(8)	111.8
Ru(3)–Ru(1)–Ru(8)	122.5	Ru(2)–Ru(1)–Ru(9)	57.5
Ru(3)–Ru(1)–Ru(9)	87.9	Ru(8)–Ru(1)–Ru(9)	54.8
Ru(2)–Ru(1)–Ru(10)	89.3	Ru(3)–Ru(1)–Ru(10)	61.1
Ru(8)–Ru(1)–Ru(10)	61.9	Ru(9)–Ru(1)–Ru(10)	57.5
Ru(2)–Ru(1)–Cc(1)	43.0(3)	Ru(3)–Ru(1)–Cc(1)	46.1(3)
Ru(8)–Ru(1)–Cc(1)	87.6(3)	Ru(9)–Ru(1)–Cc(1)	41.8(3)
Ru(10)–Ru(1)–Cc(1)	46.3(3)	Ru(2)–Ru(1)–Cbr(1)	88.8(3)
Ru(3)–Ru(1)–Cbr(1)	45.7(3)	Ru(8)–Ru(1)–Cbr(1)	147.1(3)
Ru(9)–Ru(1)–Cbr(1)	133.3(3)	Ru(10)–Ru(1)–Cbr(1)	94.6(3)
Cc(1)–Ru(1)–Cbr(1)	91.5(4)	Ru(2)–Ru(1)–C(1a)	162.7(4)
Ru(3)–Ru(1)–C(1a)	127.4(4)	Ru(8)–Ru(1)–C(1a)	77.9(4)
Ru(9)–Ru(1)–C(1a)	132.2(4)	Ru(10)–Ru(1)–C(1a)	108.0(4)
Cc(1)–Ru(1)–C(1a)	154.3(5)	Cbr(1)–Ru(1)–C(1a)	89.5(5)
Ru(2)–Ru(1)–C(1b)	72.7(3)	Ru(3)–Ru(1)–C(1b)	115.7(4)
Ru(8)–Ru(1)–C(1b)	114.2(5)	Ru(9)–Ru(1)–C(1b)	102.5(4)
Ru(10)–Ru(1)–C(1b)	158.9(4)	Cc(1)–Ru(1)–C(1b)	115.0(4)
Cbr(1)–Ru(1)–C(1b)	95.8(6)	C(1a)–Ru(1)–C(1b)	90.4(5)
Ru(1)–Ru(2)–Ru(3)	56.8	Ru(1)–Ru(2)–Ru(4)	92.5
Ru(3)–Ru(2)–Ru(4)	62.4	Ru(1)–Ru(2)–Ru(9)	63.0
Ru(3)–Ru(2)–Ru(9)	89.0	Ru(4)–Ru(2)–Ru(9)	59.4
Ru(1)–Ru(2)–Cc(1)	44.6(3)	Ru(3)–Ru(2)–Cc(1)	43.9(3)
Ru(4)–Ru(2)–Cc(1)	47.9(3)	Ru(9)–Ru(2)–Cc(1)	45.1(3)
Ru(1)–Ru(2)–Cbr(2)	135.7(3)	Ru(3)–Ru(2)–Cbr(2)	84.8(3)
Ru(4)–Ru(2)–Cbr(2)	46.6(3)	Ru(9)–Ru(2)–Cbr(2)	98.5(4)
Cc(1)–Ru(2)–Cbr(2)	93.0(4)	Ru(1)–Ru(2)–C(2a)	105.4(3)
Ru(3)–Ru(2)–C(2a)	91.1(4)	Ru(4)–Ru(2)–C(2a)	132.4(4)
Ru(9)–Ru(2)–C(2a)	165.7(4)	Cc(1)–Ru(2)–C(2a)	133.0(5)
Cbr(2)–Ru(2)–C(2a)	95.8(5)	Ru(1)–Ru(2)–C(2b)	121.3(4)
Ru(3)–Ru(2)–C(2b)	177.1(4)	Ru(4)–Ru(2)–C(2b)	120.4(4)
Ru(9)–Ru(2)–C(2b)	91.9(5)	Cc(1)–Ru(2)–C(2b)	136.8(6)
Cbr(2)–Ru(2)–C(2b)	97.8(5)	C(2a)–Ru(2)–C(2b)	87.4(6)
Ru(1)–Ru(3)–Ru(2)	62.6	Ru(1)–Ru(3)–Ru(4)	92.7
Ru(2)–Ru(3)–Ru(4)	57.0	Ru(1)–Ru(3)–Ru(10)	60.2
Ru(2)–Ru(3)–Ru(10)	89.8	Ru(4)–Ru(3)–Ru(10)	63.1
Ru(1)–Ru(3)–Cc(1)	48.0(3)	Ru(2)–Ru(3)–Cc(1)	44.0(3)
Ru(4)–Ru(3)–Cc(1)	44.7(3)	Ru(10)–Ru(3)–Cc(1)	45.9(3)
Ru(1)–Ru(3)–Cbr(1)	47.6(4)	Ru(2)–Ru(3)–Cbr(1)	91.6(4)
Ru(4)–Ru(3)–Cbr(1)	139.5(4)	Ru(10)–Ru(3)–Cbr(1)	95.3(4)
Cc(1)–Ru(3)–Cbr(1)	95.3(5)	Ru(1)–Ru(3)–C(3a)	124.1(4)
Ru(2)–Ru(3)–C(3a)	173.1(3)	Ru(4)–Ru(3)–C(3a)	118.6(4)
Ru(10)–Ru(3)–C(3a)	92.4(5)	Cc(1)–Ru(3)–C(3a)	137.8(6)
Cbr(1)–Ru(3)–C(3a)	94.6(5)	Ru(1)–Ru(3)–C(3b)	124.2(5)
Ru(2)–Ru(3)–C(3b)	85.5(5)	Ru(4)–Ru(3)–C(3b)	107.2(4)
Ru(10)–Ru(3)–C(3b)	170.2(4)	Cc(1)–Ru(3)–C(3b)	128.8(5)
Cbr(1)–Ru(3)–C(3b)	93.5(6)	C(3a)–Ru(3)–C(3b)	91.3(7)
Ru(2)–Ru(4)–Ru(3)	60.7	Ru(2)–Ru(4)–Ru(5)	123.9
Ru(3)–Ru(4)–Ru(5)	111.6	Ru(2)–Ru(4)–Ru(9)	62.1
Ru(3)–Ru(4)–Ru(9)	89.5	Ru(5)–Ru(4)–Ru(9)	62.3
Ru(2)–Ru(4)–Ru(10)	88.4	Ru(3)–Ru(4)–Ru(10)	57.0
Ru(5)–Ru(4)–Ru(10)	55.3	Ru(9)–Ru(4)–Ru(10)	57.9
Ru(2)–Ru(4)–Cc(1)	46.1(3)	Ru(3)–Ru(4)–Cc(1)	43.0(3)
Ru(5)–Ru(4)–Cc(1)	88.4(3)	Ru(9)–Ru(4)–Cc(1)	46.5(3)

Table 5 (continued)

(A) Angles around ruthenium atoms			
Ru(10)–Ru(4)–Cc(1)	42.3(3)	Ru(2)–Ru(4)–Cbr(2)	46.6(3)
Ru(3)–Ru(4)–Cbr(2)	83.6(3)	Ru(5)–Ru(4)–Cbr(2)	156.0(4)
Ru(9)–Ru(4)–Cbr(2)	100.9(3)	Ru(10)–Ru(4)–Cbr(2)	132.5(3)
Cc(1)–Ru(4)–Cbr(2)	91.3(4)	Ru(2)–Ru(4)–C(4a)	120.7(3)
Ru(3)–Ru(4)–C(4a)	75.1(3)	Ru(5)–Ru(4)–C(4a)	107.4(3)
Ru(9)–Ru(4)–C(4a)	157.1(3)	Ru(10)–Ru(4)–C(4a)	99.3(3)
Cc(1)–Ru(4)–C(4a)	116.7(4)	Cbr(2)–Ru(4)–C(4a)	94.1(5)
Ru(2)–Ru(4)–C(4b)	125.2(4)	Ru(3)–Ru(4)–C(4b)	163.9(4)
Ru(5)–Ru(4)–C(4b)	78.4(4)	Ru(9)–Ru(4)–C(4b)	106.5(4)
Ru(10)–Ru(4)–C(4b)	133.5(4)	Cc(1)–Ru(4)–C(4b)	152.8(5)
Cbr(2)–Ru(4)–C(4b)	91.5(5)	C(4a)–Ru(4)–C(4b)	90.1(5)
Ru(4)–Ru(5)–Ru(6)	122.2	Ru(4)–Ru(5)–Ru(7)	111.0
Ru(6)–Ru(5)–Ru(7)	61.3	Ru(4)–Ru(5)–Ru(9)	54.5
Ru(6)–Ru(5)–Ru(9)	88.0	Ru(7)–Ru(5)–Ru(9)	57.0
Ru(4)–Ru(5)–Ru(10)	61.5	Ru(6)–Ru(5)–Ru(10)	61.3
Ru(7)–Ru(5)–Ru(10)	89.2	Ru(9)–Ru(5)–Ru(10)	57.4
Ru(4)–Ru(5)–Cc(2)	86.9(3)	Ru(6)–Ru(5)–Cc(2)	46.6(3)
Ru(7)–Ru(5)–Cc(2)	43.1(3)	Ru(9)–Ru(5)–Cc(2)	41.5(3)
Ru(10)–Ru(5)–Cc(2)	46.1(3)	Ru(4)–Ru(5)–Cbr(3)	153.4(4)
Ru(6)–Ru(5)–Cbr(3)	46.0(3)	Ru(7)–Ru(5)–Cbr(3)	84.9(3)
Ru(9)–Ru(5)–Cbr(3)	132.3(3)	Ru(10)–Ru(5)–Cbr(3)	99.0(3)
Cc(2)–Ru(5)–Cbr(3)	91.4(4)	Ru(4)–Ru(5)–C(5a)	79.2(4)
Ru(6)–Ru(5)–C(5a)	125.3(3)	Ru(7)–Ru(5)–C(5a)	163.4(4)
Ru(9)–Ru(5)–C(5a)	133.4(4)	Ru(10)–Ru(5)–C(5a)	107.3(4)
Cc(2)–Ru(5)–C(5a)	153.3(5)	Cbr(3)–Ru(5)–C(5a)	91.1(5)
Ru(4)–Ru(5)–C(5b)	111.9(3)	Ru(6)–Ru(5)–C(5b)	118.5(3)
Ru(7)–Ru(5)–C(5b)	74.4(3)	Ru(9)–Ru(5)–C(5b)	102.1(3)
Ru(10)–Ru(5)–C(5b)	159.1(3)	Cc(2)–Ru(5)–C(5b)	116.6(4)
Cbr(3)–Ru(5)–C(5b)	92.5(5)	C(5a)–Ru(5)–C(5b)	89.8(5)
Ru(5)–Ru(6)–Ru(7)	62.2	Ru(5)–Ru(6)–Ru(8)	93.1
Ru(7)–Ru(6)–Ru(8)	56.6	Ru(5)–Ru(6)–Ru(10)	60.6
Ru(7)–Ru(6)–Ru(10)	89.3	Ru(8)–Ru(6)–Ru(10)	63.5
Ru(5)–Ru(6)–Cc(2)	48.6(3)	Ru(7)–Ru(6)–Cc(2)	43.5(3)
Ru(8)–Ru(6)–Cc(2)	44.5(3)	Ru(10)–Ru(6)–Cc(2)	45.8(3)
Ru(5)–Ru(6)–Cbr(3)	46.8(3)	Ru(7)–Ru(6)–Cbr(3)	86.1(3)
Ru(8)–Ru(6)–Cbr(3)	136.9(3)	Ru(10)–Ru(6)–Cbr(3)	99.0(4)
Cc(2)–Ru(6)–Cbr(3)	94.2(4)	Ru(5)–Ru(6)–C(6a)	116.3(4)
Ru(7)–Ru(6)–C(6a)	176.7(5)	Ru(8)–Ru(6)–C(6a)	121.3(4)
Ru(10)–Ru(6)–C(6a)	87.4(5)	Cc(2)–Ru(6)–C(6a)	133.2(6)
Cbr(3)–Ru(6)–C(6a)	94.9(5)	Ru(5)–Ru(6)–C(6b)	131.3(3)
Ru(7)–Ru(6)–C(6b)	91.9(3)	Ru(8)–Ru(6)–C(6b)	106.4(3)
Ru(10)–Ru(6)–C(6b)	166.6(3)	Cc(2)–Ru(6)–C(6b)	133.7(5)
Cbr(3)–Ru(6)–C(6b)	94.4(5)	C(6a)–Ru(6)–C(6b)	91.1(5)
Ru(5)–Ru(7)–Ru(6)	56.5	Ru(5)–Ru(7)–Ru(8)	93.1
Ru(6)–Ru(7)–Ru(8)	62.4	Ru(5)–Ru(7)–Ru(9)	63.6
Ru(6)–Ru(7)–Ru(9)	89.1	Ru(8)–Ru(7)–Ru(9)	60.2
Ru(5)–Ru(7)–Cc(2)	45.1(3)	Ru(6)–Ru(7)–Cc(2)	43.8(3)
Ru(8)–Ru(7)–Cc(2)	48.0(3)	Ru(9)–Ru(7)–Cc(2)	45.3(3)
Ru(5)–Ru(7)–Cbr(4)	137.7(4)	Ru(6)–Ru(7)–Cbr(4)	88.5(4)
Ru(8)–Ru(7)–Cbr(4)	46.3(4)	Ru(9)–Ru(7)–Cbr(4)	96.4(4)
Cc(2)–Ru(7)–Cbr(4)	93.7(5)	Ru(5)–Ru(7)–C(7a)	103.6(5)
Ru(6)–Ru(7)–C(7a)	85.7(5)	Ru(8)–Ru(7)–C(7a)	126.8(4)
Ru(9)–Ru(7)–C(7a)	166.8(5)	Cc(2)–Ru(7)–C(7a)	128.3(6)
Cbr(4)–Ru(7)–C(7a)	95.6(6)	Ru(5)–Ru(7)–C(7b)	121.3(4)

(continued)

Table 5 (continued)

(A) Angles around ruthenium atoms			
Ru(6)–Ru(7)–C(7b)	175.3(4)	Ru(8)–Ru(7)–C(7b)	122.2(4)
Ru(9)–Ru(7)–C(7b)	93.3(5)	Cc(2)–Ru(7)–C(7b)	138.4(5)
Cbr(4)–Ru(7)–C(7b)	95.2(6)	C(7a)–Ru(7)–C(7b)	91.1(7)
Ru(1)–Ru(8)–Ru(6)	110.8	Ru(1)–Ru(8)–Ru(7)	122.6
Ru(6)–Ru(8)–Ru(7)	61.0	Ru(1)–Ru(8)–Ru(9)	61.7
Ru(6)–Ru(8)–Ru(9)	89.0	Ru(7)–Ru(8)–Ru(9)	61.4
Ru(1)–Ru(8)–Ru(10)	54.7	Ru(6)–Ru(8)–Ru(10)	56.7
Ru(7)–Ru(8)–Ru(10)	87.9	Ru(9)–Ru(8)–Ru(10)	57.5
Ru(1)–Ru(8)–Cc(2)	87.3(3)	Ru(6)–Ru(8)–Cc(2)	43.1(3)
Ru(7)–Ru(8)–Cc(2)	46.1(3)	Ru(9)–Ru(8)–Cc(2)	46.0(3)
Ru(10)–Ru(8)–Cc(2)	41.8(3)	Ru(1)–Ru(8)–Cbr(4)	150.9(4)
Ru(6)–Ru(8)–Cbr(4)	87.5(4)	Ru(7)–Ru(8)–Cbr(4)	46.5(3)
Ru(9)–Ru(8)–Cbr(4)	97.6(3)	Ru(10)–Ru(8)–Cbr(4)	133.5(4)
Cc(2)–Ru(8)–Cbr(4)	92.0(5)	Ru(1)–Ru(8)–C(8a)	79.7(3)
Ru(6)–Ru(8)–C(8a)	162.1(3)	Ru(7)–Ru(8)–C(8a)	126.4(3)
Ru(9)–Ru(8)–C(8a)	108.8(3)	Ru(10)–Ru(8)–C(8a)	134.0(3)
Cc(2)–Ru(8)–C(8a)	154.7(4)	Cbr(4)–Ru(8)–C(8a)	89.1(5)
Ru(1)–Ru(8)–C(8b)	112.6(4)	Ru(6)–Ru(8)–C(8b)	73.2(4)
Ru(7)–Ru(8)–C(8b)	116.9(4)	Ru(9)–Ru(8)–C(8b)	158.3(4)
Ru(10)–Ru(8)–C(8b)	101.6(4)	Cc(2)–Ru(8)–C(8b)	115.6(5)
Cbr(4)–Ru(8)–C(8b)	93.9(5)	C(8a)–Ru(8)–C(8b)	89.5(5)
Ru(1)–Ru(9)–Ru(2)	59.5	Ru(1)–Ru(9)–Ru(4)	89.8
Ru(2)–Ru(9)–Ru(4)	58.4	Ru(1)–Ru(9)–Ru(5)	114.6
Ru(2)–Ru(9)–Ru(5)	121.1	Ru(4)–Ru(9)–Ru(5)	63.2
Ru(1)–Ru(9)–Ru(7)	121.3	Ru(2)–Ru(9)–Ru(7)	179.0
Ru(4)–Ru(9)–Ru(7)	121.9	Ru(5)–Ru(9)–Ru(7)	59.4
Ru(1)–Ru(9)–Ru(8)	63.5	Ru(2)–Ru(9)–Ru(8)	122.3
Ru(4)–Ru(9)–Ru(8)	130.2	Ru(5)–Ru(9)–Ru(8)	89.6
Ru(7)–Ru(9)–Ru(8)	58.4	Ru(1)–Ru(9)–Ru(10)	57.3
Ru(2)–Ru(9)–Ru(10)	90.3	Ru(4)–Ru(9)–Ru(10)	65.0
Ru(5)–Ru(9)–Ru(10)	57.4	Ru(7)–Ru(9)–Ru(10)	90.7
Ru(8)–Ru(9)–Ru(10)	65.3	Ru(1)–Ru(9)–Cc(1)	42.5(3)
Ru(2)–Ru(9)–Cc(1)	44.1(3)	Ru(4)–Ru(9)–Cc(1)	47.2(3)
Ru(5)–Ru(9)–Cc(1)	89.5(3)	Ru(7)–Ru(9)–Cc(1)	136.8(3)
Ru(8)–Ru(9)–Cc(1)	95.8(2)	Ru(10)–Ru(9)–Cc(1)	46.2(3)
Ru(1)–Ru(9)–Cc(2)	89.2(3)	Ru(2)–Ru(9)–Cc(2)	136.4(3)
Ru(4)–Ru(9)–Cc(2)	95.5(3)	Ru(5)–Ru(9)–Cc(2)	42.7(3)
Ru(7)–Ru(9)–Cc(2)	44.5(3)	Ru(8)–Ru(9)–Cc(2)	47.0(3)
Ru(10)–Ru(9)–Cc(2)	46.2(3)	Cc(1)–Ru(9)–Cc(2)	92.3(4)
Ru(1)–Ru(9)–C(9a)	81.5(4)	Ru(2)–Ru(9)–C(9a)	84.6(4)
Ru(4)–Ru(9)–C(9a)	140.6(4)	Ru(5)–Ru(9)–C(9a)	153.9(4)
Ru(7)–Ru(9)–C(9a)	94.9(4)	Ru(8)–Ru(9)–C(9a)	79.3(3)
Ru(10)–Ru(9)–C(9a)	134.0(3)	Cc(1)–Ru(9)–C(9a)	114.9(5)
Cc(2)–Ru(9)–C(9a)	122.6(4)	Ru(1)–Ru(9)–C(9b)	156.2(4)
Ru(2)–Ru(9)–C(9b)	96.9(4)	Ru(4)–Ru(9)–C(9b)	78.3(4)
Ru(5)–Ru(9)–C(9b)	78.4(4)	Ru(7)–Ru(9)–C(9b)	82.3(4)
Ru(8)–Ru(9)–C(9b)	139.2(4)	Ru(10)–Ru(9)–C(9b)	131.3(4)
Cc(1)–Ru(9)–C(9b)	122.6(4)	Cc(2)–Ru(9)–C(9b)	112.2(5)
C(9a)–Ru(9)–C(9b)	94.7(5)	Ru(1)–Ru(10)–Ru(3)	58.6
Ru(1)–Ru(10)–Ru(4)	89.8	Ru(3)–Ru(10)–Ru(4)	59.9
Ru(1)–Ru(10)–Ru(5)	130.4	Ru(3)–Ru(10)–Ru(5)	122.3
Ru(4)–Ru(10)–Ru(5)	63.2	Ru(1)–Ru(10)–Ru(6)	122.5
Ru(3)–Ru(10)–Ru(6)	178.3(1)	Ru(4)–Ru(10)–Ru(6)	120.9
Ru(5)–Ru(10)–Ru(6)	58.2	Ru(1)–Ru(10)–Ru(8)	63.4
Ru(3)–Ru(10)–Ru(8)	121.5	Ru(4)–Ru(10)–Ru(8)	114.4

Table 5 (continued)

(A) Angles around ruthenium atoms			
Ru(5)–Ru(10)–Ru(8)	89.6	Ru(6)–Ru(10)–Ru(8)	59.8
Ru(1)–Ru(10)–Ru(9)	65.2	Ru(3)–Ru(10)–Ru(9)	90.8
Ru(4)–Ru(10)–Ru(9)	57.1	Ru(5)–Ru(10)–Ru(9)	65.3
Ru(6)–Ru(10)–Ru(9)	90.9	Ru(8)–Ru(10)–Ru(9)	57.3
Ru(1)–Ru(10)–Cc(1)	47.0(3)	Ru(3)–Ru(10)–Cc(1)	44.8(3)
Ru(4)–Ru(10)–Cc(1)	42.8(3)	Ru(5)–Ru(10)–Cc(1)	95.8(3)
Ru(6)–Ru(10)–Cc(1)	136.9(3)	Ru(8)–Ru(10)–Cc(1)	89.2(3)
Ru(9)–Ru(10)–Cc(1)	46.1(3)	Ru(1)–Ru(10)–Cc(2)	95.4(3)
Ru(3)–Ru(10)–Cc(2)	136.7(3)	Ru(4)–Ru(10)–Cc(2)	88.9(3)
Ru(5)–Ru(10)–Cc(2)	47.2(3)	Ru(6)–Ru(10)–Cc(2)	45.0(3)
Ru(8)–Ru(10)–Cc(2)	42.4(3)	Ru(9)–Ru(10)–Cc(2)	45.9(3)
Cc(1)–Ru(10)–Cc(2)	92.0(4)	Ru(1)–Ru(10)–C(10a)	76.1(3)
Ru(3)–Ru(10)–C(10a)	92.3(3)	Ru(4)–Ru(10)–C(10a)	152.1(3)
Ru(5)–Ru(10)–C(10a)	143.2(3)	Ru(6)–Ru(10)–C(10a)	86.8(3)
Ru(8)–Ru(10)–C(10a)	80.9(3)	Ru(9)–Ru(10)–C(10a)	132.0(3)
Cc(1)–Ru(10)–C(10a)	119.3(4)	Cc(2)–Ru(10)–C(10a)	116.0(4)
Ru(1)–Ru(10)–C(10b)	141.3(4)	Ru(3)–Ru(10)–C(10b)	85.1(4)
Ru(4)–Ru(10)–C(10b)	81.9(3)	Ru(5)–Ru(10)–C(10b)	78.5(4)
Ru(6)–Ru(10)–C(10b)	93.5(4)	Ru(8)–Ru(10)–C(10b)	152.9(4)
Ru(9)–Ru(10)–C(10b)	133.9(3)	Cc(1)–Ru(10)–C(10b)	115.9(4)
Cc(2)–Ru(10)–C(10b)	121.9(5)	C(10a)–Ru(10)–C(10b)	94.1(4)
(B) Angles about μ_6-carbide atoms			
Ru(1)–Cc(1)–Ru(2)	92.5(4)	Ru(1)–Cc(1)–Ru(3)	85.9(4)
Ru(2)–Cc(1)–Ru(3)	92.1(5)	Ru(1)–Cc(1)–Ru(4)	177.6(6)
Ru(2)–Cc(1)–Ru(4)	86.0(3)	Ru(3)–Cc(1)–Ru(4)	92.3(4)
Ru(1)–Cc(1)–Ru(9)	95.6(4)	Ru(2)–Cc(1)–Ru(9)	90.8(4)
Ru(3)–Cc(1)–Ru(9)	176.6(6)	Ru(4)–Cc(1)–Ru(9)	86.2(4)
Ru(1)–Cc(1)–Ru(10)	86.7(3)	Ru(2)–Cc(1)–Ru(10)	178.2(6)
Ru(3)–Cc(1)–Ru(10)	89.4(4)	Ru(4)–Cc(1)–Ru(10)	94.9(4)
Ru(9)–Cc(1)–Ru(10)	87.7(4)	Ru(5)–Cc(2)–Ru(6)	84.9(4)
Ru(5)–Cc(2)–Ru(7)	91.8(4)	Ru(6)–Cc(2)–Ru(7)	92.7(5)
Ru(5)–Cc(2)–Ru(8)	176.3(7)	Ru(6)–Cc(2)–Ru(8)	92.4(4)
Ru(7)–Cc(2)–Ru(8)	85.8(4)	Ru(5)–Cc(2)–Ru(9)	95.8(4)
Ru(6)–Cc(2)–Ru(9)	177.1(7)	Ru(7)–Cc(2)–Ru(9)	90.2(4)
Ru(8)–Cc(2)–Ru(9)	87.1(4)	Ru(5)–Cc(2)–Ru(10)	86.7(4)
Ru(6)–Cc(2)–Ru(10)	89.2(4)	Ru(7)–Cc(2)–Ru(10)	177.5(5)
Ru(8)–Cc(2)–Ru(10)	95.8(5)	Ru(9)–Cc(2)–Ru(10)	88.0(5)
(C) Terminal Ru–C–O angles			
Ru(1)–C(1a)–O(1a)	174.2(13)	Ru(1)–C(1b)–O(1b)	175.9(9)
Ru(2)–C(2a)–O(2a)	177.6(11)	Ru(2)–C(2b)–O(2b)	178.5(9)
Ru(3)–C(3a)–O(3a)	179.2(13)	Ru(3)–C(3b)–O(3b)	176.4(14)
Ru(4)–C(4a)–O(4a)	175.4(9)	Ru(4)–C(4b)–O(4b)	178.4(12)
Ru(5)–C(5a)–O(5a)	176.6(10)	Ru(5)–C(5b)–O(5b)	173.1(10)
Ru(6)–C(6a)–O(6a)	174.0(12)	Ru(6)–C(6b)–O(6b)	178.0(11)
Ru(7)–C(7a)–O(7a)	179.2(14)	Ru(7)–C(7b)–O(7b)	178.6(13)
Ru(8)–C(8a)–O(8a)	172.8(11)	Ru(8)–C(8b)–O(8b)	172.7(2)
Ru(9)–C(9a)–O(9a)	173.9(10)	Ru(9)–C(9b)–O(9b)	174.8(11)
Ru(10)–C(10a)–O(10a)	170.8(9)	Ru(10)–C(10b)–O(10b)	175.2(9)
(D) Angles involving μ-CO ligands			
Ru(1)–Cbr(1)–Ru(3)	86.7(5)	Ru(1)–Cbr(1)–Obr(1)	134.2(9)
Ru(3)–Cbr(1)–Obr(1)	139.0(10)	Ru(2)–Cbr(2)–Ru(4)	86.8(4)
Ru(2)–Cbr(2)–Obr(2)	136.6(10)	Ru(4)–Cbr(2)–Obr(2)	136.5(10)
Ru(5)–Cbr(3)–Ru(6)	87.1(5)	Ru(5)–Cbr(3)–Obr(3)	136.0(8)
Ru(6)–Cbr(3)–Obr(3)	136.8(8)	Ru(7)–Cbr(4)–Ru(8)	87.3(5)
Ru(7)–Cbr(4)–Obr(4)	135.3(11)	Ru(8)–Cbr(4)–Obr(4)	137.4(10)

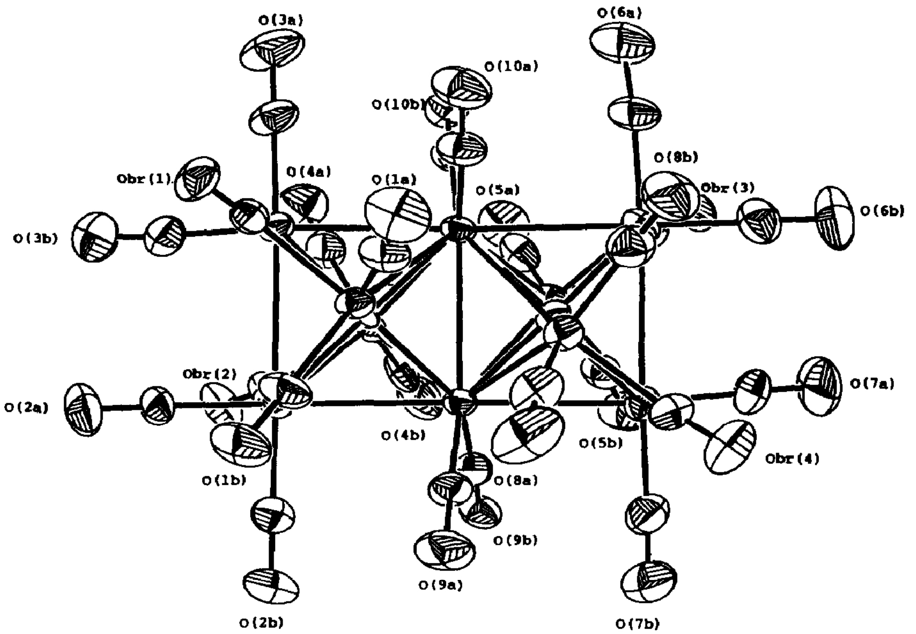

Fig. 5. The $Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}$ anion, projected onto its equatorial plane. Note the D_2 symmetry (C_2 axes horizontal, vertical and perpendicular to the plane of projection).

(1) The alternate "short" Ru(apical)–Ru(fused) distances, Ru(1)–Ru(10) = 2.863(1), Ru(4)–Ru(9) = 2.849(1), Ru(5)–Ru(10) = 2.873(1) and Ru(8)–Ru(9) = 2.866(1) Å; average = 2.863 Å.

(2) The unique Ru(fused)–Ru(fused) bond, Ru(9)–Ru(10) = 2.872(1) Å.

(3) The diequatorial Ru(non-fused)–Ru(fused) distances, Ru(2)–Ru(9) = 2.925(2), Ru(3)–Ru(10) = 2.889(2), Ru(6)–Ru(10) = 2.892(2), and Ru(7)–Ru(9) = 2.901(2) Å; average = 2.902 Å.

(4) The two non-fused diequatorial distances, Ru(2)–Ru(3) = 2.931(2) and Ru(6)–Ru(7) = 2.950(2) Å; average = 2.941 Å.

(5) The non-bridged Ru(apical)–Ru(equatorial, non-fused) distances, Ru(1)–Ru(2) = 2.986(1), Ru(4)–Ru(3) = 2.979(2), Ru(5)–Ru(7) = 2.976(2) and Ru(8)–Ru(6) = 2.990(2) Å; average = 2.983 Å.

Interestingly, the two μ_6-carbide atoms, labelled Cc(1) and Cc(2), are not located in perfectly centered positions within their Ru_6 cavities. The individual Ru–C distances fall naturally into three non-overlapping sets.

(1) The shortest are the Ru(equatorial, non-fused)–Cc distances, with Ru(2)–Cc(1) = 2.037(10), Ru(3)–Cc(1) = 2.035(12), Ru(6)–Cc(2) = 2.044(11) and Ru(7)–Cc(2) = 2.034(12) Å; average = 2.038 Å.

(2) Intermediate are the Ru(equatorial, fused)–Cc distances, with Ru(9)–Cc(1) = 2.071(12), Ru(10)–Cc(1) = 2.074(10), Ru(9)–Cc(2) = 2.063(11) and Ru(10)–Cc(2) = 2.073(12) Å; average = 2.070 Å.

(3) The longest are the Ru(axial)–Cc distances, with Ru(1)–Cc(1) = 2.098(9), Ru(4)–Cc(1) = 2.096(9), Ru(5)–Cc(2) = 2.110(10) and Ru(8)–Cc(2) = 2.098(10) Å; average = 2.101 Å.

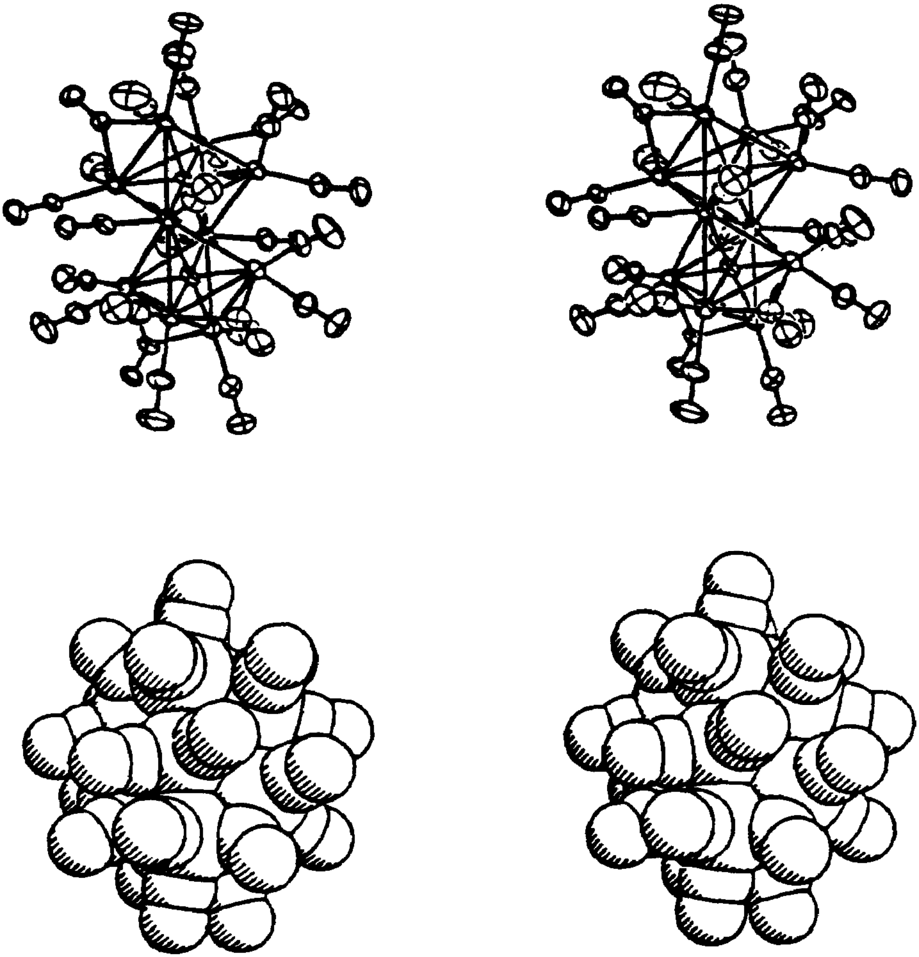

Fig. 6. Stereoscopic views of the $Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}$ anion (ORTEP-II diagram at the top and space-filling model at the bottom).

Other distances within the anion are internally consistent with Ru–CO(terminal) = 1.845(14)–1.894(12) Å (average = 1.869 Å), Ru–CO(bridging) = 2.018(11)–2.082(14)Å (average = 2.044 Å), C–O(terminal) = 1.131(13)–1.169(18) Å (average = 1.151 Å) and C–O(bridging) = 1.160(13)–1.181(17) Å (average = 1.174 Å).

Supplementary data available

A table of observed and calculated structure factor amplitudes and complete tables of interatomic distances and angles for the cation are available upon request from M.R.C.

Discussion

The $Os_{10}C(CO)_{24}^{2-}$ dianion is based upon the symmetrically tetracapped octahedron (T_d symmetry) and has 134 valence electrons as predicted by the Wade–Mingos rules [6,7]. The decanuclear species $Rh_{10}S(CO)_{22}^{2-}$ [8], $Rh_{10}P(CO)_{22}^{3-}$ [9] and $Rh_{10}As(CO)_{22}^{3-}$ [10] are each based upon the more open bicapped square antiprismatic (D_{4d} symmetry) arrangement; each is associated with 142 valence electrons as predicted by Lauher [11]. Using a similar treatment, Ciani and Sironi [12] predicted 134 valence electrons for a D_{2h} structure in which two edge-fused octahedra also have apical–apical M–M bonds.

The present 138 valence electron dianion, $Ru_{10}C_2(CO)_{24}^{2-}$, has four electrons more that the 134 valence electrons needed for a stable D_{2h} arrangement. We suggest that these are involved in antibonding Ru–Ru orbitals which are principally localized on the apical ruthenium atoms (Ru(1), Ru(4), Ru(5), Ru(8)). The contacts Ru(1) ··· Ru(8) = 3.138(2) Å and Ru(4) ··· Ru(5) = 3.122(2) Å are thus regarded as non-bonding and the metal atom framework distorts from D_{2h} to D_2 symmetry because of repulsions between the pairs of apical ruthenium atoms. The twist about the edge-fused Ru(9)–Ru(10) bond is best measured by the dihedral angle of 12.8° between planes defined by Ru(1)–Ru(4)–(center of Ru(9)–Ru(10) bond) and Ru(5)–Ru(8)–(center of Ru(9)–Ru(10) bond).

While the edge-fused bisoctahedral core is unique in metal carbonyl clusters, a similar arrangement has been found for the gadolinium atoms in the decanuclear bis(dicarbide) complexes $Gd_{10}(\mu_6\text{-}C_2)_2(\mu\text{-}Cl)_{18}$ and $[Gd_{10}(\mu_6\text{-}C_2)_2(\mu\text{-}Cl)_{17}]_\infty$ [13–15].

Some comments on the severely disordered crystal structure of $[NEt_4^+]_2[Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}]$

We had earlier collected X-ray diffraction data on the $[NEt_4^+]$ salt of the $[Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}]$ anion. While we were unable to completely solve this structure, we now understand why. We believe that a brief summary of our progress will be of interest to crystallographers working in this area.

Crystals were twinned, but a set of rather weak diffraction data were collected. Crystals belong to the monoclinic system, space group $P2_1/c$, with $a = 11.00(1)$, $b = 13.29(1)$, $c = 19.72(1)$ Å, $\beta = 97.49(6)°$, $V = 2858(4)$ Å^3, D(meas'd) = 2.27(2) g cm^{-3} and D(calc'd) = 2.286 g cm^{-3} for $M = 1967$ and $Z = 2$. Direct methods (MULTAN) yielded the positions of the ten ruthenium atoms. The cluster lies about a site of C_i ($\bar{1}$) symmetry (at $\frac{1}{2}$, 0, $\frac{1}{2}$). The use of difference-Fourier maps led to the location of the two symmetry-related carbide atoms and of the nitrogen atom of the unique NEt_4^+ cation (in a general position). This information is collected in Table 6. The 'R-value' at this stage was 22% for 1829 reflections ($2\theta = 3.5$–$35.0°$, Mo-K_α).

Table 6

Heavy atom locations in $[NEt_4^+]_2[Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}]$

Atom[a]	x	y	z
Ru(1)	0.293	0.075	0.525
Ru(2)	0.454	0.251	0.505
Ru(3)	0.476	0.132	0.637
Ru(4)	0.669	0.126	0.551
Ru(9)	0.489	0.053	0.437
Cc(1)	0.503	0.089	0.538
N	−0.002	−0.018	0.162

[a] Numbering scheme as in Fig. 3. Other atoms of the $Ru_{10}C_2$ cluster are related by the transformation $[1-x, -y, 1-z]$.

Efforts to locate other atoms led to positions for some, but not all, carbonyl ligands and exceedingly high thermal parameters.

Looking back at the structure of the $[Ru_{10}(\mu_6\text{-}C)_2(CO)_{20}(\mu\text{-}CO)_4^{2-}]$ ion as its $[PPh_3PCH_2CH_2PPh_3^{2+}]$ salt, we now understand our misfortunes. Spectroscopic studies show that the anion is static in solution; one may reasonably assume that the geometry of the anion is the same in the $[NEt_4^+]$ salt as it is in the $[Ph_3PCH_2CH_2PPh_3^{2+}]$ salt. However, the structure in the latter salt has D_2 symmetry and clearly has no inversion center (see Figs. 3 and 5). In the $[NEt_4^+]$ salt, the anion lies about an inversion center and the metal atom framework has apparent $D_2 \times i$ $(= D_{2h})$ symmetry. The fully resolved structure would be the composite of that of Fig. 3 overlapping that of the image related by inversion. The equatorial carbonyl ligands should not be affected drastically, but axial and bridging carbonyls will be scrambled. Such disorder presumably also scrambles the ethyl ligands of the NEt_4^+ cations.

Acknowledgements

We thank Professor J.R. Shapley for providing the crystals.

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