Notes

Nuclear Magnetic Resonance Evidence for Three Different Isomers of $[Ru_3(\mu\text{-}H)(\mu\text{-}bzim)(CO)_9(PPh_3)]$ (bzim = benzimidazolate). Crystal Structure of $[Ru_3(\mu\text{-}H)(\mu\text{-}bzim)(CO)_{10}]\cdot Me_2CO$†

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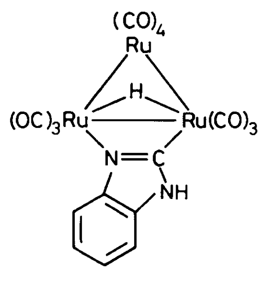
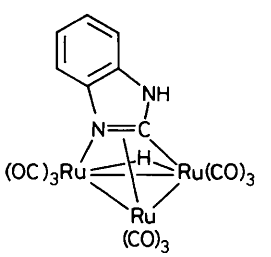
The reaction of $[Ru_3(CO)_{12}]$ with benzimidazole (Hbzim) gave $[Ru_3(\mu\text{-}H)(\mu\text{-}bzim)(CO)_{10}]$ (**1a**). The spectroscopic (fast atom bombardment mass, n.m.r., and i.r.) and analytical data were not enough to assign its structure unequivocally, which was suggested by its reactivity with PPh_3 {which led to a mixture of three isomers of $[Ru_3(\mu\text{-}H)(\mu\text{-}bzim)(CO)_9(PPh_3)]$, with the minor component (8%) having the PPh_3 ligand on the Ru atom unbridged by the bzim moiety} and was confirmed by an *X*-ray structure determination of the acetone solvate. Crystals of (**1a**)·Me_2CO are triclinic, space group $P\bar{1}$ with $Z = 2$ in a unit cell of dimensions $a = 12.995(9)$, $b = 13.197(10)$, $c = 7.708(12)$ Å, $\alpha = 92.47(3)$, $\beta = 97.56(4)$, and $\gamma = 91.94(3)°$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.0667$ for 2 151 observed reflections. It comprises a triangle of Ru atoms in which the longest edge, 2.949(3) Å, is doubly bridged by a hydride and by a bzim ligand bonded to the two Ru atoms through adjacent C and N atoms of the imidazole moiety.

Recently we have reported[1] that the reaction of $[Ru_3(CO)_{12}]$ with benzimidazole (Hbzim) gives $[Ru_3(\mu\text{-}H)(\mu\text{-}bzim)(CO)_{10}]$ (**1**), proposing for it the structure (**1a**) on the basis of ^1H n.m.r. and i.r. spectra and C, H, and N analysis. However, fast atom bombardment mass spectrometry (f.a.b.m.s.), which normally gives the molecular ions of carbonyl clusters,[2] gave the highest peak at *m*/*z* 676 (^{102}Ru) and the successive loss of nine carbonyl groups. This might be assigned to a parent compound such as $[Ru_3(\mu\text{-}H)(\mu_3\text{-}bzim)(CO)_9]$ ($M = 673.44$, isotopic mixture). This, and the recent publication of the structure of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}PhC{=}NPh)(CO)_9]$,[3] suggested (**1b**) as a possible structure for (**1**), since it also fits with the spectroscopic and analytical data.

This note reports our efforts to elucidate the correct structure of compound (**1**), both by chemical and *X*-ray diffraction methods.



(**1a**)



(**1b**)

Results and Discussion

If compound (**1**) has the structure (**1b**), the π bond between the C=N moiety and the ruthenium atom should be very labile and could be easily replaced by a strong ligand such as PPh_3 to give a compound with a structure of the type (**2a**), which has the PPh_3 ligand on the ruthenium atom unbridged by the bzim ligand. However, the reaction of (**1**) with PPh_3 in a 1:1 mol ratio, at room temperature, gave a mixture of three isomers in a ratio of 2.5:9:1, as indicated by the ^1H and ^{31}P n.m.r. spectra (Figure 1). Since the hydride resonances of the two major components of the mixture are doublets (δ −13.8, *J* 10.3; −14.02, *J* 11.3 Hz), the corresponding structures should be of types (**2b**) and (or) (**2c**). In addition, the hydride of (**2a**) is not

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† 1,2-(μ-Benzimidazolato-C^2N^1)-1,1,1,2,2,2,3,3,3,3-decacarbonyl-1,2-μ-hydrido-*triangulo*-triruthenium–acetone (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

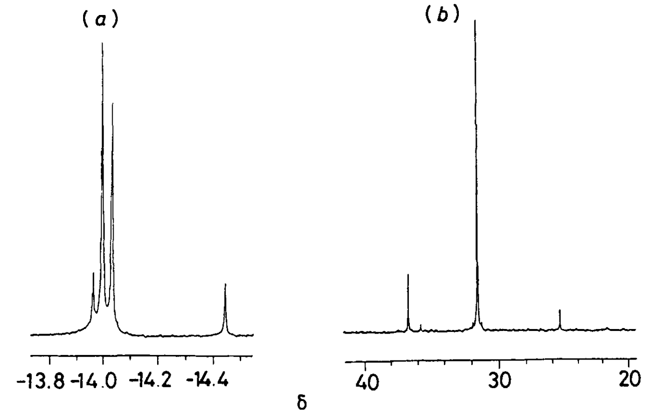
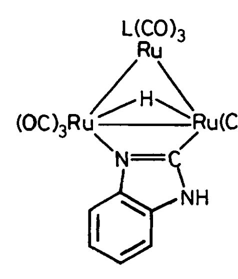
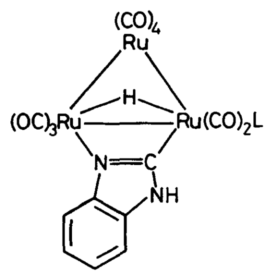


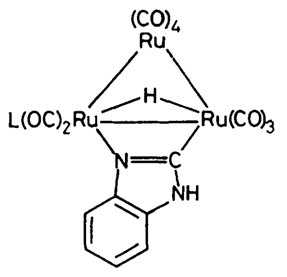
Figure 1. N.m.r. spectra (CDCl$_3$) of [Ru$_3$(μ-H)(μ-bzim)(CO)$_9$(PPh$_3$)] (mixture of isomers): (*a*) ^{1}H n.m.r. spectrum in the hydride region; (*b*) ^{31}P-{^{1}H} n.m.r. spectrum



(2a)



(2b)



(2c)

expected to be coupled to phosphorus, whereas the coupling constant ^2J(H–Ru–P) of (**2b**) and (**2c**) should be *ca.* 10—12 Hz, as reported for other ruthenium carbonyl clusters.[4]

So far, these data indicate that (**1a**) is the most probable structure for compound (**1**). This tentative assignment was finally confirmed by an *X*-ray structure determination of the acetone solvate.

Description of the Crystal Structure of [Ru$_3$(μ-H)(μ-bzim)(CO)$_{10}$]·Me$_2$CO, (**1a**)·Me$_2$CO.—The crystal structure of compound (**1a**)·Me$_2$CO consists of trinuclear clusters and acetone molecules of solvation (Figure 2). Selected bond distances and angles are listed in Table 1. The structure shows a triangular array of Ru atoms of unequal length [2.858(4), 2.880(4), and 2.949(3) Å] bonded to ten terminal carbonyl groups [four to the Ru(3) and three to the Ru(1) and Ru(2) atoms], and to a benzimidazolate(1−) ligand which bridges the longest Ru(1)–Ru(2) edge through the N(1) and C(11) atoms of the imidazolate moiety [Ru(2)–N(1) 2.10(1) and Ru(1)–C(11) 2.07(1) Å]. The Ru(1)–C(11)–N(1)–Ru(2) bridge is nearly perpendicular to the metal cluster [the dihedral angle between the mean plane through the bridge and the metal triangle is 102.9(3)°]. The Ru(1)–Ru(2) edge of the cluster is also bridged by a hydride ligand on the opposite side with respect to the former bridge. The Ru(1)–H(1)–Ru(2) plane forms a dihedral angle of 124(7)° with the metal triangle and of 133(7)° with the bzim bridge. The presence of the hydride results, as expected, in opening of the Ru(2)–Ru(1)–C(2) and Ru(1)–Ru(2)–C(5) angles [117.9(7) and 116.2(6)°]. The whole bzim ligand is planar, the maximum deviation from the mean plane passing through it being 0.04(2) Å for C(13) with atoms Ru(1) and Ru(2) deviating by 0.101(3) and 0.128(3) Å.

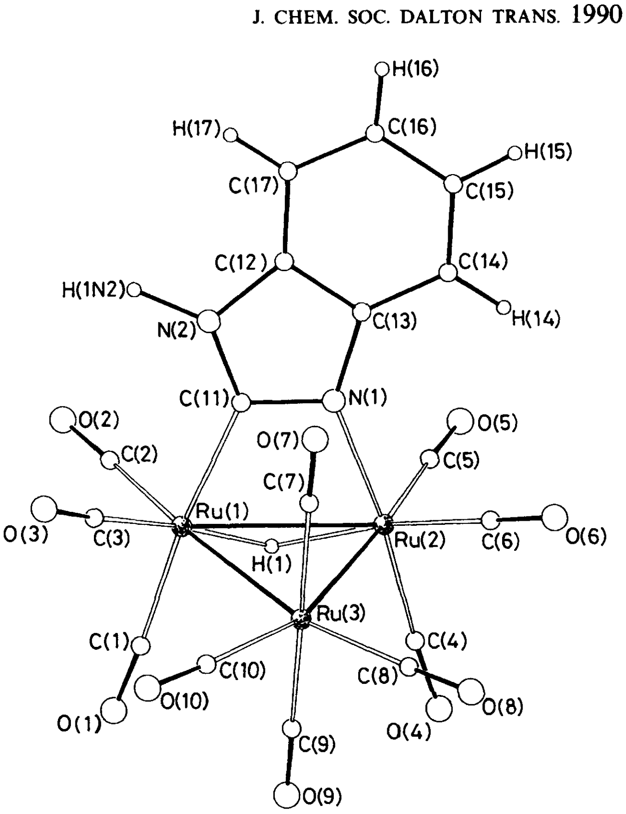


Figure 2. View of the structure of the compound [Ru$_3$(μ-H)(μ-bzim)(CO)$_{10}$] (**1a**) with the atomic numbering scheme

Worthy of mention is the hydrogen bond involving the hydrogen atom at N(2) of the imidazole moiety and the oxygen atom O(11) of the acetone molecule of solvation [N(2) ··· O(11) 2.81(2), H(1N2) ··· O(11) 1.76(14) Å; N(2)–H(1N2)–O(11) 147(11)°].

Experimental

General procedures, measurements, and the synthesis of compound (**1a**) were as previously reported.[1] Crystals of (**1a**)·Me$_2$CO were obtained by cooling to *ca.* 0 °C a saturated solution of (**1a**) in acetone–water (3:1).

Reaction of [Ru$_3$(μ-H)(μ-bzim)(CO)$_{10}$] (**1a**) *with* PPh$_3$.—Compound (**1a**) (200 mg, 0.285 mmol) and PPh$_3$ (80 mg, 0.305 mmol) were stirred in dichloromethane (15 cm^3) at room temperature for 24 h. Vacuum evaporation to dryness gave a yellow-orange solid which was washed with hexane (two 5-cm^3 portions) and vacuum-dried (226 mg, 85%) (Found: C, 43.9; H, 2.7; N, 2.7. Calc. for $C_{34}H_{21}N_2O_9PRu_3$: C, 43.7; H, 2.3; N, 3.0%). The ^{1}H and ^{31}P-{^{1}H} n.m.r. spectra of the product (Figure 1) showed that it was a mixture of three isomers (see above).

Determination of the Crystal Structure of [Ru$_3$(μ-H)(μ-bzim)(CO)$_{10}$]·Me$_2$CO, (**1a**)·Me$_2$CO.—A crystal of approximate dimensions 0.15 × 0.20 × 0.27 mm was selected for the *X*-ray analysis.

Table 1. Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for compound (**1a**)

Ru(1)–Ru(2)	2.949(3)	Ru(3)–C(7)	1.93(2)
Ru(1)–Ru(3)	2.880(4)	Ru(3)–C(8)	1.92(2)
Ru(2)–Ru(3)	2.858(4)	Ru(3)–C(9)	1.93(2)
Ru(1)–C(11)	2.07(1)	Ru(3)–C(10)	1.91(2)
Ru(2)–N(1)	2.10(1)	C(1)–O(1)	1.13(2)
N(1)–C(11)	1.34(2)	C(2)–O(2)	1.11(3)
C(11)–N(2)	1.36(2)	C(3)–O(3)	1.14(2)
N(2)–C(12)	1.40(2)	C(4)–O(4)	1.15(2)
C(12)–C(13)	1.38(2)	C(5)–O(5)	1.17(3)
N(1)–C(13)	1.41(2)	C(6)–O(6)	1.17(3)
Ru(1)–C(1)	1.96(2)	C(7)–O(7)	1.14(2)
Ru(1)–C(2)	1.90(3)	C(8)–O(8)	1.15(3)
Ru(1)–C(3)	1.91(2)	C(9)–O(9)	1.16(2)
Ru(2)–C(4)	1.90(2)	C(10)–O(10)	1.16(2)
Ru(2)–C(5)	1.89(2)	Ru(1)–H(1)	1.60(13)
Ru(2)–C(6)	1.87(2)	Ru(2)–H(1)	1.77(14)
Ru(2)–Ru(1)–Ru(3)	58.71(8)	Ru(1)–Ru(2)–C(5)	116.2(6)
Ru(1)–Ru(2)–Ru(3)	59.43(8)	Ru(1)–Ru(3)–C(7)	86.5(5)
Ru(1)–Ru(3)–Ru(2)	61.86(8)	Ru(1)–Ru(3)–C(9)	88.6(6)
C(11)–Ru(1)–Ru(2)	66.6(3)	Ru(1)–Ru(3)–C(10)	97.6(6)
C(11)–Ru(1)–Ru(3)	88.9(4)	Ru(2)–Ru(3)–C(7)	85.0(5)
N(1)–Ru(2)–Ru(1)	67.9(3)	Ru(2)–Ru(3)–C(8)	99.4(6)
N(1)–Ru(2)–Ru(3)	88.8(3)	Ru(2)–Ru(3)–C(9)	89.8(6)
Ru(1)–C(11)–N(1)	115.2(8)	C(7)–Ru(3)–C(8)	92.6(8)
Ru(1)–C(11)–N(2)	135.1(9)	C(7)–Ru(3)–C(10)	93.2(8)
N(1)–C(11)–N(2)	109.7(10)	C(8)–Ru(3)–C(10)	101.2(10)
Ru(2)–N(1)–C(11)	110.2(8)	C(8)–Ru(3)–C(9)	91.0(8)
Ru(2)–N(1)–C(13)	142.0(8)	C(9)–Ru(3)–C(10)	90.7(8)
C(11)–N(1)–C(13)	107.6(10)	C(11)–N(2)–C(12)	109(1)
C(11)–Ru(1)–C(2)	88.4(7)	N(2)–C(12)–C(13)	106(1)
C(11)–Ru(1)–C(3)	91.3(6)	N(2)–C(12)–C(17)	132(1)
C(2)–Ru(1)–C(3)	95.8(7)	C(13)–C(12)–C(17)	122(1)
C(1)–Ru(1)–C(2)	92.9(8)	N(1)–C(13)–C(12)	108(1)
C(1)–Ru(1)–C(3)	96.1(7)	N(1)–C(13)–C(14)	130(1)
Ru(3)–Ru(1)–C(3)	86.7(7)	C(12)–C(13)–C(14)	122(1)
Ru(3)–Ru(1)–C(1)	89.4(5)	Ru(1)–C(1)–O(1)	174(2)
Ru(2)–Ru(1)–C(1)	106.2(4)	Ru(1)–C(2)–O(2)	174(2)
Ru(2)–Ru(1)–C(2)	117.9(7)	Ru(1)–C(3)–O(3)	177(1)
N(1)–Ru(2)–C(5)	89.1(7)	Ru(2)–C(4)–O(4)	176(2)
N(1)–Ru(2)–C(6)	92.7(7)	Ru(2)–C(5)–O(5)	177(1)
C(5)–Ru(2)–C(6)	97.0(8)	Ru(2)–C(6)–O(6)	177(2)
C(4)–Ru(2)–C(5)	93.4(8)	Ru(3)–C(7)–O(7)	174(2)
C(4)–Ru(2)–C(6)	93.0(7)	Ru(3)–C(8)–O(8)	173(2)
Ru(3)–Ru(2)–C(4)	88.3(6)	Ru(3)–C(9)–O(9)	179(2)
Ru(3)–Ru(2)–C(6)	87.0(8)	Ru(3)–C(10)–O(10)	177(2)
Ru(1)–Ru(2)–C(4)	105.5(5)	Ru(1)–H(1)–Ru(2)	122(8)

Crystal data. $C_{17}H_6N_2O_{10}Ru_3 \cdot C_3H_6O$, $M = 759.53$, triclinic, space group $P\bar{1}$, $a = 12.995(9)$, $b = 13.197(10)$, $c = 7.708(12)$ Å, $\alpha = 92.47(3)$, $\beta = 97.56(4)$, $\gamma = 91.94(3)$°, $U = 1\,308(2)$ Å^3 (by least-squares refinement from the θ values of 30 accurately measured reflections with θ in the range 9—16°, $\lambda = 0.710\,73$ Å), $Z = 2$, $D_c = 1.928$ g cm^{-3}, $F(000) = 732$, μ(Mo-K_α) = 17.33 cm^{-1}.

Data collection and processing. A Siemens AED single-crystal diffractometer (θ–2θ scan mode, niobium-filtered Mo-K_α radiation) was employed. All reflections with θ in the range 3—24° were measured; of 3 500 independent reflections, 2 151, having $I > 2\sigma(I)$, were considered observed and used in the analyses. The individual profiles were analyzed according to Lehmann and Larsen.[5] The intensity of one standard reflection was measured after each 50 reflections as a general check on crystal and instrument stability; a decline to about 30% of the initial intensity was observed during the time required to collect the data. A correction for this decay was applied, but not for absorption.

Table 2. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for the non-hydrogen atoms of compound (**1a**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	1 624(1)	1 614(1)	2 477(2)
Ru(2)	2 628(1)	3 654(1)	2 523(2)
Ru(3)	1 343(1)	2 834(1)	−545(3)
O(1)	−636(8)	1 908(10)	3 175(23)
O(2)	2 042(12)	342(10)	5 616(28)
O(3)	1 215(9)	−225(9)	−91(22)
O(4)	979(9)	5 171(8)	3 112(22)
O(5)	3 961(12)	4 412(11)	5 925(25)
O(6)	3 623(12)	5 005(10)	63(23)
O(7)	3 314(9)	1 951(10)	−1 695(21)
O(8)	1 521(14)	4 549(13)	−3 057(25)
O(9)	−584(9)	3 716(10)	810(22)
O(10)	−27(10)	1 279(12)	−2 976(23)
N(1)	3 672(7)	2 500(7)	2 204(19)
N(2)	3 888(8)	852(7)	2 118(21)
C(1)	176(12)	1 821(10)	2 824(29)
C(2)	1 887(13)	859(11)	4 521(40)
C(3)	1 337(11)	461(12)	877(32)
C(4)	1 571(12)	4 578(11)	2 850(28)
C(5)	3 462(13)	4 101(12)	4 629(32)
C(6)	3 246(14)	4 506(12)	1 051(33)
C(7)	2 604(12)	2 272(12)	−1 166(27)
C(8)	1 437(14)	3 951(16)	−2 041(33)
C(9)	145(13)	3 388(13)	323(27)
C(10)	473(13)	1 884(15)	−2 067(33)
C(11)	3 197(9)	1 590(9)	2 258(23)
C(12)	4 870(10)	1 312(10)	2 072(27)
C(13)	4 729(10)	2 342(10)	2 080(27)
C(14)	5 560(10)	3 041(11)	2 135(27)
C(15)	6 506(11)	2 647(13)	2 003(29)
C(16)	6 646(11)	1 597(14)	1 931(30)
C(17)	5 828(10)	910(12)	1 997(30)
O(11)	3 032(11)	−1 088(11)	2 589(22)
C(18)	3 347(14)	−1 922(14)	2 914(30)
C(19)	2 556(19)	−2 719(17)	3 071(36)
C(20)	4 383(19)	−2 186(18)	2 978(37)

Structure solution and refinement. Patterson and Fourier methods, full-matrix least-squares refinements with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms except those of the acetone molecule. The hydride and the hydrogen at N(2) were clearly localized in the final Fourier difference map and refined isotropically, the remaining ones were placed at their calculated positions (C–H 1.00 Å) and refined 'riding' on the corresponding carbon atoms. A weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement with $K = 1.462$ and $g = 0.0007$. Final R and R' values were 0.0667 and 0.0727 respectively. The SHELX system of computer programs was used.[6] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 7. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 2. All calculations were carried out on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna and on the GOULD POWERNODE 6040 of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

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