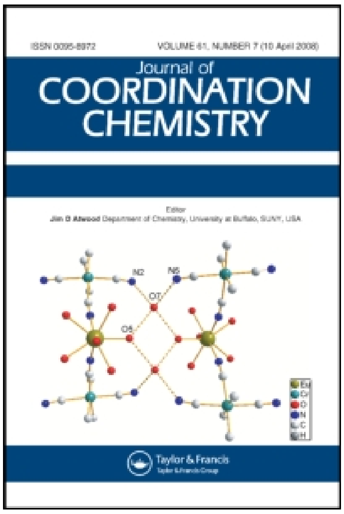

**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# THE CRYSTAL AND MOLECULAR STRUCTURE OF $Ru_3(CO)_9(PPh_3)_3$

Nicholas E. Leadbeater[a]; Paul R. Raithby[b]
[a] Department of Chemistry, King's College London Strand, London, UK [b] Department of Chemistry, University of Cambridge, Cambridge, UK

**To cite this Article** Leadbeater, Nicholas E. and Raithby, Paul R.(2001) 'THE CRYSTAL AND MOLECULAR STRUCTURE OF $Ru_3(CO)_9(PPh_3)_3$', Journal of Coordination Chemistry, 53: 4, 311 — 316
**To link to this Article: DOI:** 10.1080/00958970108022617
**URL:** http://dx.doi.org/10.1080/00958970108022617

J. Coord. Chem., 2001, Vol. 53, pp. 311–316
Reprints available directly from the publisher
Photocopying permitted by license only

# THE CRYSTAL AND MOLECULAR STRUCTURE OF $Ru_3(CO)_9(PPh_3)_3$

NICHOLAS E. LEADBEATER[a,*] and PAUL R. RAITHBY[b]

[a]*Department of Chemistry, King's College London Strand, London, WC2R 2LS, UK;* [b]*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK*

*(Received 2 May 2000)*

The synthesis of tertiary phosphine and phosphite substituted derivatives of $M_3(CO)_{12}$ {M = Ru(**1a**) Os(**1b**)} is discussed and the X-ray crystal and molecular structure of the *tris*-triphenylphosphine substituted ruthenium cluster $Ru_3(CO)_9(PPh_3)_3$ (**2a**) is reported. Complex **2a** crystallises in the monoclinic space group $P2_1/n$ with cell parameters $a = 14.180(9)$, $b = 21.644(14)$, $c = 18.248(10)$ Å, $\beta = 92.52(5)°$, $V = 5595(6)$ Å$^3$, $Z = 4$. The structure was solved by full-matrix least-squares methods based on $F^2$. The refinement converged at $R1 = 0.0564$, $wR2 = 0.2125$ for 4857 observed data $[F > 4\sigma(F)]$.

*Keywords*: Ruthenium; Cluster carbonyls; Phosphine ligands; X-ray structure

## INTRODUCTION

The synthesis and structural chemistry of substituted trinuclear ruthenium and osmium clusters has been the subject of a considerable number of reports in the literature [1]. Of particular note are the *mono*-, *bis*- and *tris*-substituted derivatives of $M_3(CO)_{12}$ (M = Ru (**1a**) Os (**1b**)) containing group 15 donor ligands. Although the crystal and molecular structures of a number of these substituted derivatives have been determined, that of one of the archetypal and best-known complexes in this series, $Ru_3(CO)_9(PPh_3)_3$ (**2a**), has not. In this paper we report and discuss the X-ray crystal and molecular structure of **2a**. This adds valuable information to the chemical literature and helps in the rationalisation of the reaction chemistry of the

---

*Corresponding author.

frequently cited **2a** and in the comparison of its chemistry with that of other substituted derivatives [2].

## EXPERIMENTAL

The *tris*-substituted cluster $Ru_3(CO)_9(PPh_3)_3$ (**2a**) was prepared by photolysis of $Ru_3(CO)_{12}$ (**1a**) in ethyl acetate with three stoichiometric equivalents of $PPh_3$ [3]. Suitable single-crystals of **2a** were grown from a dichloromethane-hexane solution by slow evaporation. Crystal data: $C_{63}H_{45}O_9$- $P_3Ru_3$, red blocks, crystal dimensions 0.35 × 0.25 × 0.21 mm, monoclinic, $P2_1/n$, $a = 14.180(9)$, $b = 21.644(14)$, $c = 18.248(10)$ Å, $\beta = 92.52(5)°$, $V = 5595(6)$ Å$^3$, $D_{calc} = 1.593$ Mg m$^{-3}$, $Z = 4$, $F(000) = 2688$, MoK$\alpha$ radiation, $\lambda = 0.71073$ Å, $\mu$(MoK$\alpha$) $= 0.943$ mm$^{-1}$, $T = 153(2)$ K. Stoe-Siemens AED diffractometer, 7199 reflections collected in the range $3.56 \leq \theta \leq 21.50$, 6383 unique absorption corrected data ($R_{int} = 0.031$). The structure was solved by direct methods (Ru atoms) (SHELXTL PLUS) [4] and Fourier difference syntheses and refined with Ru, C and O atoms anisotropic by full-matrix least-squares based on $F^2$ (SHELXL 93) [5]. Hydrogen atoms were placed in idealised positions and allowed to ride on the relevant carbon atoms. In the final cycles of refinement a weighting scheme was introduced which produced a flat analysis of variance [6]. The refinement converged at $R1 = 0.0564$, $wR2 = 0.2125$ for 4857 observed data $[F > 4\sigma(F)]$, and $R1 = 0.0809$ and $wR^2 = 0.2455$ (all data), goodness of fit on $F^2 = 1.172$, max, min peak in final difference map $= 1.105$, $-1.166$ e Å$^{-3}$, max $\Delta/\sigma = 0.001$.

## RESULTS AND DISCUSSION

There are a number of preparative routes to tertiary phosphine, $PR_3$, and phosphite, $P(OR)_3$, ($R$ = alkyl, aryl) substituted trinuclear ruthenium and osmium carbonyl clusters. Thermolysis of the binary metal carbonyl **1a** or **1b** with $PR_3$ or $P(OR)_3$ in a high boiling point solvent leads generally to the *tris*-substituted product but often together with polysubstitution, further transformation of the ligand after complexation to the metal cluster, or both [7, 8]. By using a radical ion initiator such as sodium diphenylketyl, it is possible to form *mono*-, *bis*- and *tris*-phosphine and phosphite substituted selectively from **1a** and **1b** simply by changing the stoichiometric ratio of the binary cluster carbonyl to ligand [7, 9]. The efficiency of the reaction decreases with higher substitution and, at the same time, steric and statistical factors will disfavour higher substitution. We have found that another highly selective route to substituted clusters is photolysis [3]. Irradiating an ethyl acetate or acetonitrile solution of **1a** or **1b** together with the appropriate stoichiometric equivalents of ligand, using a broad-band UV source leads to excellent yields of substituted products. We therefore use broad-band UV photolysis to prepare substituted ruthenium clusters, such as **2a**, in high yield.

## The X-ray Crystal and Molecular Structure of $Ru_3(CO)_9(PPh_3)_3$ (2a)

A view of the molecular structure of **2a** is shown in Figure 1 and selected bond lengths and angles given in Table I. Unlike many other reported molecular structures of phosphine-substituted ruthenium clusters, disorder is not evident in the structure of **2a**. The disorder problem characteristic of these complexes is one which can be resolved by using a model in which the outer atoms of the ligands (O of CO, P of $PR_3$) form a polyhedron which remains unaltered while the metal core may take up two positions related by a 60° rotation within this polyhedron [10]. A similar model has been used to describe the two-fold disorder found in other trinuclear clusters such as $Fe_3(CO)_{12}$ [11] and $Fe_3(\mu_3\text{-As})(CO)_9$ [12]. The reason that **2a** is not

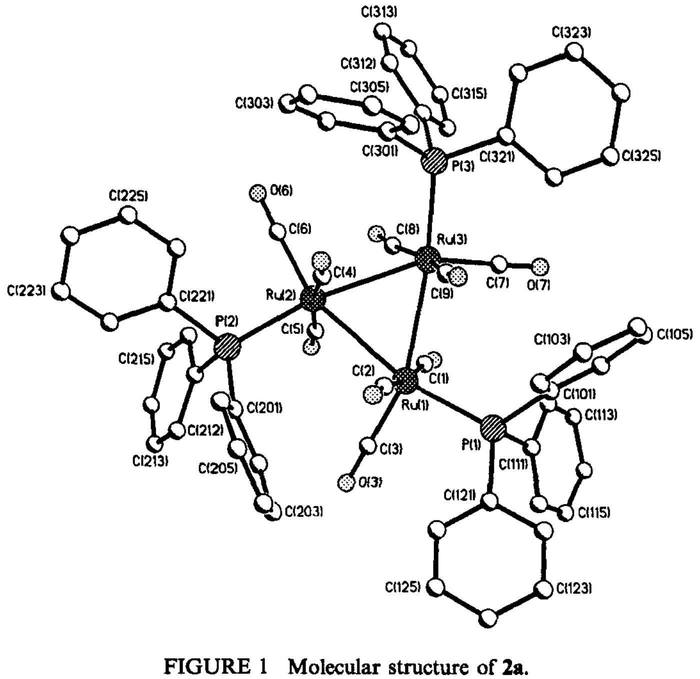

FIGURE 1 Molecular structure of **2a**.

TABLE I Selected bond lengths (Å) and angles (°) for **2a**

| | | | |
|---|---|---|---|
| Ru(1)—C(3) | 1.88(2) | Ru(1)—C(1) | 1.94(2) |
| Ru(1)—C(2) | 1.95(2) | Ru(1)—P(1) | 2.349(4) |
| Ru(1)—Ru(3) | 2.868(2) | Ru(1)—Ru(2) | 2.890(2) |
| Ru(2)—C(6) | 1.86(2) | Ru(2)—C(5) | 1.90(2) |
| Ru(2)—C(4) | 1.94(2) | Ru(2)—P(2) | 2.341(4) |
| Ru(2)—Ru(3) | 2.864(2) | Ru(3)—C(7) | 1.88(2) |
| Ru(3)—C(8) | 1.91(2) | Ru(3)—C(9) | 1.93(2) |
| Ru(3)—P(3) | 2.333(4) | | |
| Ru(3)—Ru(1)—Ru(2) | 59.65(5) | Ru(2)—Ru(3)—Ru(1) | 60.56(5) |
| Ru(3)—Ru(2)—Ru(1) | 59.79 (4) | P(1)—Ru(1)—Ru(3) | 106.10(11) |
| P(1)—Ru(1)—Ru(2) | 158.90(10) | P(2)—Ru(2)—Ru(1) | 109.45(10) |
| P(2)—Ru(2)—Ru(3) | 164.75(10) | P(3)—Ru(3)—Ru(2) | 111.01(11) |
| P(3)—Ru(3)—Ru(1) | 163.25(10) | C(1)—Ru(1)—Ru(3) | 76.9(4) |
| C(1)—Ru(1)—Ru(2) | 97.1(4) | C(2)—Ru(1)—Ru(3) | 94.4(4) |
| C(2)—Ru(1)—Ru(2) | 77.0(4) | C(3)—Ru(1)—Ru(2) | 101.2(4) |
| C(4)—Ru(2)—Ru(3) | 80.1(4) | C(4)—Ru(2)—Ru(1) | 96.0(4) |
| C(5)—Ru(2)—Ru(3) | 94.8(4) | C(5)—Ru(2)—Ru(1) | 72.1(4) |
| C(6)—Ru(2)—Ru(3) | 98.7(4) | C(6)—Ru(2)—Ru(1) | 151.5(4) |
| C(7)—Ru(3)—Ru(2) | 151.3(5) | C(7)—Ru(3)—Ru(1) | 97.1(5) |
| C(8)—Ru(3)—Ru(2) | 72.7(4) | C(8)—Ru(3)—Ru(1) | 96.5(4) |
| C(9)—Ru(3)—Ru(2) | 93.8(4) | C(9)—Ru(3)—Ru(1) | 81.3(4) |

disordered could be because the data were collected at 153 K. That the disorder in the other structures is a dynamic phenomenon is indicated by the results of a variable temperature X-ray study of $Ru_3(CO)_{11}(CN^tBu)$, where at 298 K the populations of the two sites is 14:86 but at 133 K is 6:94 [13].

Complex **2a** crystallises in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. The molecular structure is similar to, but not isomorphous with, that of the osmium analogue $Os_3(CO)_9(PPh_3)_3$ (**2b**) [14]. Structurally, **2a** is related to that of **1a** by replacement of an equatorial CO ligand on each metal with a tertiary phosphine ligand, thereby minimising the steric interactions between them. It is both isostructural and isomorphic with the *tris*-trimethylphosphine substituted analogue $Ru_3(CO)_9(PMe_3)_3$ (**3a**) [14]. The three Ru—Ru bond lengths in **2a** are not identical but similar, the maximum difference being 0.022 Å. The average metal-metal bond distance of 2.874(2) Å may be compared to that in **3a** {2.860(1) Å} and that in the parent **1a** {2.851(1) Å}. Of interest is that, in $Ru_3(CO)_{11}(PPh_3)$ (**4a**) [15], the Ru—Ru bond lengths differ considerably, that *cis* to the triphenylphosphine ligand being lengthened significantly {2.907(3) Å} whilst the other two are very similar to those in **2a** {2.876(3) Å}.

Although the metal-metal bonds are not perturbed greatly on substitution of three CO groups in **1a** by $PPh_3$, there is a considerable distortion of the $M_3L_{12}$ molecule from the $D_{3h}$ symmetry found in **1a**, towards the energetically more favourable $D_3$ symmetry. This has also been observed in other *tris*-substituted trinuclear clusters [16]. This distortion relieves the steric pressures arising from the interactions between the axial and equatorial CO ligands that can no longer be achieved by M—M bond lengthening as found in the monosubstituted complex **4a**. In **2b**, distortion of the $M_3L_{12}$ cluster from $D_{3h}$ symmetry is again observed but the effects are not as marked as in **2a**. The various electronic and stereochemical arguments for these distortions have been discussed in depth elsewhere [17].

The average Ru—P bond length of 2.333(4) Å in **2a** is similar to that reported for the *mono*- and *bis*- substituted analogues **4a** {2.380(6) Å} and $Ru_3(CO)_{10}(PPh_3)_2$ (**5a**) {2.365(6) Å} [9]. The geometry around the phosphorous atom is essentially tetrahedral, but distorted with the phenyl groups bent away from the metal atom to which they are bonded. A similar effect is noted in **4a** and **5a**.

The M—CO(ax) bond lengths are significantly longer that M—CO(eq), the average values being 1.93(2) and 1.87(2) Å, respectively. The average Ru—C—O(eq) bond angle is 173.7(12)° and the average Ru—C—O(ax) bond angles is 173.0(12)°. Twisting of the $M(CO)_3(PPh_3)$ units in **2a** has the effect of carrying the axial carbonyls into positions approaching semi-bridging, the average Ru—Ru—C(axial) bond angle being 77.5(4)°. This value is close to that of 73.5°, calculated using a surface force field model [17].

## *Acknowledgments*

Johnson-Matthey plc is acknowledged for the generous loan of ruthenium chloride. Advice and assistance from G.P. Shields is greatly appreciated.

## *Supplementary Data*

Positional parameters of all atoms, anisotropic displacement parameters, complete lists of bond lengths and angles, hydrogen atom coordinates and structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC deposit number 101927).

## *References*

[1] A. J. Deeming, In: *Comprehensive Organometallic Chemistry*, E. A. Abel, F. G. A. Stone and G. Wilkinson (Eds.) (Pergamon, Oxford, 1995), Vol. 7, Ch. 12.

[2] A chemical literature citation, search shows that the use and chemistry of **2a** has been cited over 100 times in the last five years.

[3] For details of the synthesis of **2a** see:, N. E. Leadbeater, *J. Organomet. Chem.* **573**, 211 (1999). Spectroscopic data: IR ($CH_2Cl_2$): $\nu_{CO}$ 2044(m), 1978(sh), 1967(s, br) $cm^{-1}$; $^1$H-NMR $\delta$ 7.43 (m) ppm; $^{31}$P-NMR $\delta$ 36.3 (s) ppm; *m/z* 1341 (calc. 1341, based on $^{101}$Ru) [NMR data reported relative to $SiMe_3$ ($d=0$) for $^1$H-NMR and to 85% $H_3PO_4$ ($d=0$) for $^{31}P\{^1H\}$-NMR spectra].

[4] G. M. Sheldrick, *SHELXTL-PLUS. A Fortran Program for Solving, Refining and Displaying Crystal Structures from Diffraction Data* (University of Göttingen, Germany, 1993).

[5] G. M. Sheldrick, *SHELXL-93. A Fortran Program for Crystal Structure Determination* (University of Göttingen, Germany, 1993).

[6] The weight, $w = 1/(\sigma^2(F_o)^2 + (0.01363P)^2 + 56.46P)$; $P = (F_o^2 + 2F_c^2)/3$.

[7] M. I. Bruce, *Coord. Chem. Rev.* **76**, 1 (1987).

[8] (a) M. I. Bruce, G. Shaw and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* 2094 (1972); (b) C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland and R. Mason, *J. Organomet. Chem.* **40**, C70 (1972).

[9] M. I. Bruce, D. C. Kehoe, J. G. Matisons, B. K. Nicholson, P. H. Reiger and M. L. Williams, *J. Chem. Soc., Chem. Comm.* 442 (1982).

[10] M. I. Bruce, B. K. Nicholson and A. H. White, *J. Organomet. Chem.* **240**, C33 (1982).

[11] F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.* **96**, 4155 (1974).

[12] L. T. J. Delbaere, L. J. Kruczynski and D. W. McBride, *J. Chem. Soc., Dalton Trans.* **307**, (1973).

[13] M. I. Bruce, C. Hughes, G. N. Pain, J. M. Patrick, B. W. Skelton and A. H. White, *J. Organomet. Chem.* **307**, 343 (1986).

[14] M. I. Bruce, M. J. Liddell, O. Bin Shawkataly, C. A. Hughes, B. W. Skelton and A. H. White, *J. Organomet. Chem.* **347**, 207 (1988).

[15] E. J. Forbes, N. Goodhand, D. L. Jones and T. A. Hamor, *J. Organomet. Chem.* **182**, 143 (1979).

[16] M. I. Bruce, M. J. Lidell, C. A. Hughes, J. M. Patrick, B. W. Skelton and A. H. White, *J. Organomet. Chem.* **347**, 181 (1988).

[17] J. W. Lauher, *J. Am. Chem. Soc.* **108**, 1521 (1986).