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Synthesis and X-ray structure of $Ru_3(CO)_6(\mu_2\text{-}CO)(\mu_2\text{-}AsPh_2)(\mu\text{-}O{=}C{-}C_{12}H_{17})$, a first example of a CO insertion reaction to a cluster-bound hydrocarbon[1]

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Abstract

Moderate heating at 81°C of $Ru_3(\mu\text{-}H)(CO)_9(C_{12}H_{17})$ (**1**) with $AsPh_3$ (1:1) for 24 h under nitrogen, afforded high yield of a purple cluster, $Ru_3(CO)_6(\mu_2\text{-}CO)(\mu_2\text{-}AsPh_2)(\mu\text{-}O{=}C{-}C_{12}H_{17})$ (**2**) which has been shown by X-ray crystallography to contain an Ru_3 cluster with a μ_2-bonding $AsPh_2$ ligand due to a cleavage of As–C bond and a new and novel type of CO insertion reaction to a cluster bound cyclic hydrocarbon. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Clusters; Ruthenium; Tripherylasine

The ready cleavage of C–E (where E=P and As) bonds in tertiary phosphine or arsine ligands attached to metal clusters has been used to make a variety of carbon bonded groups which interact with the cluster [1]. Since the discovery of the high yield synthesis $Ru_3(\mu\text{-}H)(CO)_9(C_{12}H_{17})$ [2], some chemistry of substitution reaction with group 15 ligands have been described [3,4]. The reaction between $[Ru_3(CO)_9(C_{12}H_{15})]^-$ with the trigold oxonium reagent have also been described [5]. In all the previous reactions, the mode of interaction of the cyclododecatriene (CDT) ligand have not changed. In the course of our study of the substitution of $Ru_3(\mu\text{-}H)(CO)_9(C_{12}H_{17})$ with group 15 ligands, we found an interesting example of a CO insertion reaction to the cluster bound hydrocarbon. In the present context, we seem to have uncovered a case of incipient acyl formation.

Treatment of $Ru_3(\mu\text{-}H)(CO)_9(C_{12}H_{17})$ with $AsPh_3$ in refluxing cyclohexane (81°C) for 24 h results in the high yield formation of $Ru_3(CO)_6(\mu_2\text{-}CO)(\mu_2\text{-}AsPh_2)(\mu\text{-}O{=}C{-}C_{12}H_{17})$ (**2**). Purification by column chromatography (florisil, light pet: CH_2Cl_2 70:30) afforded 80% yield of the purple complex (**2**). [IR($\nu CO(CH_2Cl_2)$ 2060 s, 2026 sh, 2016 s, 2001 s, 1976 m, 1961 m, 1609 w cm^{-1}]; ^1H-NMR: δ ($CDCl_3$) 1.0–3.3, m, 14 H, CH_2 protons; 5.4, 5.7, M, 2H, CH proton; 6.1, s, 1H, allylic CH; 7.4, m, 10H, $AsPh_2$; microanalysis (found: C, 40.55; H, 2.65; $C_{32}H_{27}O_8AsRu_3$ calcd: C, 40.88; H, 2.96%) which have been fully characterised by a single crystal X-ray study (see Appendix A).

A molecule of (**2**) is shown in Fig. 1, and important bond distances and angles are also given in the caption. There are a number of interesting features in this molecule. Complex (**2**) contains an open array of Ru_3 atoms and the mode of attachment of the CDT ligand is now much different from the usual (μ_3-2η^1,η^3) mode

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[1] Dedicated to Professor Michael I. Bruce on the occasion of his 60th birthday in recognition of his contributions to organometallic and inorganic chemistry. ObS had the privilege of being a research student under his supervision between 1982 and 1987 for a PhD, and wishes to thank him for his constant encouragement.

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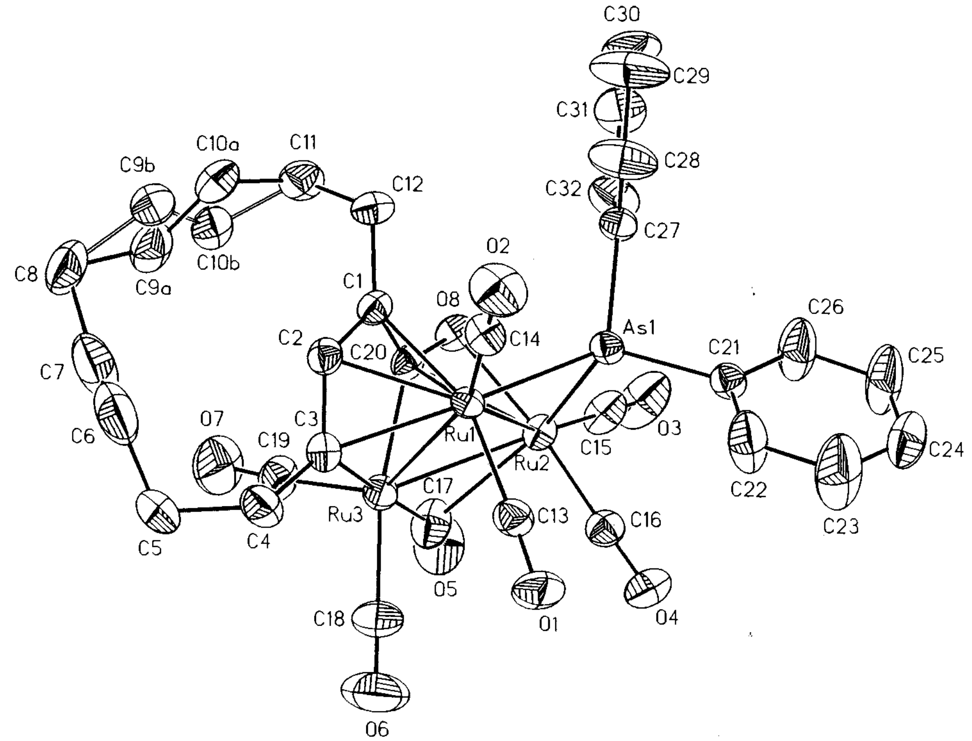

Fig. 1. Molecular structure of (**2**). Selected bond distances (Å): Ru(1)–Ru(2) 2.936(1), Ru(2)–Ru(3) 2.731(1), Ru(1)–Ru(3) 2.803(1), Ru(1)–As(1) 2.450(1), Ru(2)–As(1) 2.366(1), Ru(1)–C(2) 2.200(5), Ru(1)–C(3) 2.243(6), Ru(2)–O(8) 2.127(4), Ru(2)–C(17) 2.533(8), Ru(2)–C(20) 2.399(5), Ru(3)–C(3) 2.092(5), Ru(3)–C(17) 1.980(7), Ru(3)–C(20) 2.069(6), O(8)–C(20) 1.284(7), C(1)–C(20) 1.461(7).

found in $Ru_3(\mu\text{-}H)(CO)_9(C_{12}H_{15})$ [6], $Ru_3(CO)_8(C_{12}H_{15})(AuPP_3)_3$ [5], $HRu_3(CO)_8(C_{12}H_{15})(\mu_1\text{-}AsPh_2CH_2AsPh_2)$ [5] and $HRu_3(CO)_8(C_{12}H_{17})(PPh_3)$ [7]. The mode of bonding is now $(\mu_2\text{-}\eta^1,\eta^3)$ and in (**2**) there is no direct interaction between the CDT ligand and Ru(2).

Since complex (**2**) contains a $C_{12}H_{17}$ hydrocarbon attached to the cluster and not $C_{12}H_{15}$, we have re-examined the starting material $Ru_3(\mu\text{-}H)(CO)_9(C_{12}H_{15})$ as the other product from the reaction of CDT is $Ru_3(\mu\text{-}H)(CO)_9(C_{12}H_{17})$ [3]. However, we found that the IR matches that of $C_{12}H_{15}$ as reported in the original synthesis [3]. We have reassessed the original crystal structure of $Ru_3(\mu\text{-}H)(CO)_9(C_{12}H_{15})$ [6] and found that the reported structure is not very accurate and there were two abnormally short C=C bonds i.e. C6–C7, 1.26(7) Å, and C9–C10, 1.12(6) Å. Since this structure was solved with 1419 independent reflections and is of low accuracy, we have decided to redetermine the structure of $Ru_3(\mu\text{-}H)(CO)_9(C_{12}H_{15})$. A combination of diffractometer data, electrospray mass spectra and detailed ^1H- and ^{13}C-NMR spectroscopy shows that the complex is actually $Ru_3(\mu\text{-}H)(CO)_9(C_{12}H_{17})$ and there is no abnormal C=C bond lengths [8].

In complex (**2**), the complex is unique in that we have found an interesting first example of a CO-insertion reaction to a cluster bound cyclic hydrocarbon. The nature of formation of (**2**) is novel. The inserted CO is sideway bonded and this is not uncommon for the more conventional acyls such as $HRu_3(CO)_{10}(\mu\text{-}O{=}CNMe_2)$ [9]. The CO inserts into the CDT ligand at (C20–C1 bond length of 1.461 Å) distance and C20 is assymetrically bridging the Ru1–Ru3 bond (Ru3–C20, 2.069 Å; Ru1–C20, 2.449(5) Å). Both C20 and O8 lie across the open triangular face such that C20–O8 is both bonded to Ru2. The Ru1–Ru2 bond length (2.936(1) Å) is slightly longer and this bond is bridged by the μ_2-$AsPh_2$ ligand. This μ_2-$AsPh_2$ ligand is the outcome of the cleavage of As–C bond and the loss of one phenyl group (presumably as benzene) by abstracting the cluster bound hydride [10]. The loss of the cluster bound hydride is confirmed by ^1H-NMR. The lengthening of the Ru–Ru bond has been observed in similar $(\mu_2\text{-}ER_2)$ [E = P or As) complexes such as $HRu_3(CO)_{10}(\mu_2\text{-}PHPh)$ [11].

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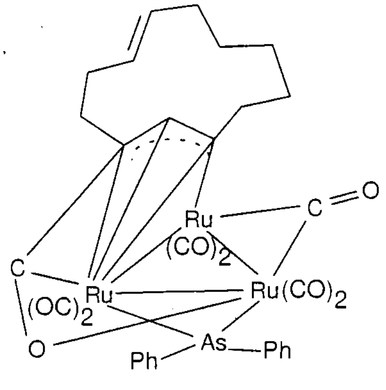
CAMBRIDGE CRYSTALLOGRAPHIC DATA CENTRE: ABSTRACT FORM

Compound Name Heptacabonyl($\mu_2$diphenylarsino)(μ-acylcyclododecatrienyl) triruthenium(0).
Diagram *(conventional chemical structural diagram)* 
Formula *(each residue to be formulated ,eg. $C_2H_3O_2^{-}\cdot Na^{+}\cdot 2H_2O$)* $Ru_3(CO)_6(\mu_2\text{-}CO)(\mu_2\text{-}AsPh_2)(\mu\text{-}O{=}C\text{-}C_{12}H_{17})$

a(A) *with estimated error* 35.618(4)		b(A) *with estimated error* 9.303(1)		c(A) *with estimated error* 23.312(3)		
alpha(deg.)*with estimated error* 90.0		beta(deg.) *with estimated error* 119.61(1)		gamma(deg.) *with estimated error* 90.0		
Space Group C2/c	Z 8	R-factor(s) R 0.062 wR 0.165	Temp(K) 293	Radiation ☒ X ☐ N		Powder Data Yes ☐ No ☑
Intensity Measurement ☐ densit. ☑ diffr. ☐ other*(specify)*			Volume(Å^3) 6715.8(14)	Mol. Weight 916.65		Mp(°C) 195
Absolute Configuration Determined ☐ Yes ☐ No		Colour Purple CAS RN		Dm (g cm^{-3}) Dx (g cm^{-3}) 1.811		
Polymorph Indicator *(eg. low-temp form)*						
Drug *(indicate, where appropriate, type of drug, activity, etc.)* ————————						
Disorder *(specify nature of disorder with reference to atom labels in coordinate list)* Disorder between C9 and C10						

Fig. 1. (*Continued*)

Appendix A. Crystal data for (2)

$Ru_3(CO)_6(\mu\text{-}CO)(\mu_2\text{-}AsPh_2)(\mu\text{-}O{=}C\text{-}C_{12}H_{17})$, [$C_{32}H_{27}AsO_8Ru_3$], $M = 915.65$, monoclinic, space group $C2/c$, $a = 35.618(4)$ Å, $b = 9.303(1)$ Å, $c = 23.312(3)$ Å, $\beta = 119.61(1)°$; $V = 6715.8$ Å^3, $Z = 8$, $D_{calc.} = 1.811$ g cm^{-3}, μ(Mo-K$_\alpha$) = 23.57 cm^{-1}, $F(000) = 3568$, $2\theta_{max} = 55°$, crystal dimensions 0.62 × 0.32 × 0.20 mm, 7614 independent reflections out of the 8957 measured reflections were used in the structure refinement. Determination of cell constants and data collection were carried out at room temperature with Mo-K$_\alpha$ radiation on a Siemens P4 diffractometer equipped with graphite monochromator. Data were recorded by a θ-2θ scans and corrected for Lorentz, polarisation and absorption effects. Absorption correction (Ψ-scans ellipsoidal) was carried out with $T_{min} = 0.1981$ and $T_{max} = 0.8398$. The structure was solved by Patterson method using SHELXS86 [12] to reveal the Ru atoms and followed by successive Fourier synthesis with SHELXL93 [13] to reveal the remaining non-hydrogen atoms and refined by the full-matrix least-squares procedure on F^2. During the course of refinement, we found unusual large thermal parameter for C9 and C10 and also unusual bond lengths associate with them. Hence the atoms C9 and C10 were split into two position C9A, C9B and C10A, C10B and their occupancies (30:70) were also refined. The residuals in the final refinement cycle were $R_1 = 0.047$, $wR_2 = 0.130$ for 5459 observed data $[|Fo| > 4\,\sigma(|Fo|)]$ and 419 parameters. The mean and maximum shift/error ratios and the maximum and minimum residual electron densities in the final refinement cycle were 0.000, -0.001 and 0.48, -0.61, respectively. The resulting structure clearly shows the formulation of the CDT ligand to be $C_{12}H_{17}$ with a double bond between C6–C7 and a single bond between C9–C10.

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