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Preliminary communication

CLUSTER CHEMISTRY

XXXX*. A NEW MODE OF ALLYL BINDING TO A METAL CLUSTER: PREPARATION AND X-RAY STRUCTURE OF $Ru_3(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_8$

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Summary

The reaction between $[Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9]^-$ and allyl chloride affords the yellow complex $Ru_3(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_8$ which is shown by an X-ray study to contain a C_3H_5 ligand symmetrically bridging two metal atoms, a hitherto undescribed mode of attachment of the allyl group to a ruthenium metal cluster.

We have briefly described the hydrogenation of $Ru_3(CO)_{10}(dppm)$ to $HRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$, and its conversion to the anion, $[Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9]^-$ (I) [1,2]. Herein we describe the reaction between I and allyl chloride.

Treatment of $Ru_3(CO)_{10}(dppm)$ in tetrahydrofuran solution with K-Selectride $[K(HBBu^s_3)]$ followed by stirring at room temperature for 5 h afforded a solution of anion I. Subsequent addition of $CH_2{=}CHCH_2Cl$ resulted in an immediate reaction (TLC), and evaporation and crystallization gave golden-yellow crystals of $Ru_3(C_3H_5)(PPhCH_2PPh_2)(CO)_8$ (II). The IR spectrum contains $\nu(CO)$ bands consistent with the presence of both terminal and bridging carbonyl ligands. Complex II is relatively insoluble, and informative ^1H NMR spectra were not obtained.

We have carried out a single-crystal X-ray diffraction study of II to determine the mode of attachment of the allylic group to the cluster.

Crystal data. $C_{30}H_{22}O_8P_2Ru_3$, $M = 875.7$, Triclinic, space group $P\bar{1}$; a

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*For Part XXXIX, see Ref. 14.

11.661(4), b 11.914(4), c 12.029(2) Å, α 80.70(2), β 81.77(2), γ 69.79(4)°, U 1554.9 Å^3, D_m 1.88, D_c 1.87 g cm^{-3} for $Z = 2$, $F(000)$ 856 electrons, λ(Mo-K_α) 0.7107 Å, μ(Mo-K_α) 15.26 cm^{-1}. Specimen: 0.14 × 0.10 × 0.08 mm. Data: 4184 unique reflections were collected in the range $2.4 < 2\theta < 46°$ on an Enraf—Nonius CAD-4 diffractometer; the 3936 having $I > 2.5\sigma(I)$ were used in the refinement after correction for absorption.

Structural determination. The structure was solved by direct methods (SHELX [3]) to give the ruthenium atom positions, with all other non-hydrogen atoms being revealed in subsequent difference fourier syntheses. The phenyl rings were included as rigid groups (C—C 1.395 Å), hydrogen atoms for the methylene group and phenyl rings were given calculated positions (C—H 0.97 and 1.08 Å, respectively) with separate group temperature factors. Hydrogen atoms of the allyl ligand were located from a difference fourier synthesis and were refined with fixed bond lengths (C—H 0.97 Å). The structure was refined by blocked full-matrix least-squares techniques (with all non-hydrogen atoms and non-phenyl carbons anisotropic) to $R = 0.027$, $R_w = 0.034$ where $w = 3.5049\,[\sigma^2(F) + 0.000074F^2]^{-1}$. A final differences synthesis showed no peak > 0.8 eÅ^{-3} *.

A molecule of II is shown in Fig. 1, which also gives selected bond lengths and angles. The three ruthenium atoms define an isosceles triangle with the Ru(1)—Ru(2) and Ru(1)—Ru(3) edges being of equal length (2.853(1) Å), while Ru(2)—Ru(3) is slightly longer at 2.887(1) Å. The Ru_3 core is capped by the dephenylated $PPhCH_2PPh_2$ ligand in the same fashion as found earlier in $H_2Ru_3(\mu_3\text{-}PPhCH_2PPh_2)_2(CO)_6$ [4] and $MRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9$-$(PPh_3)$ (M = Cu, Ag and Au) [5]; the bond parameters between these complexes do not differ significantly. Each ruthenium is bonded to two terminal CO ligands, the remaining two μ-CO groups asymmetrically bridging the Ru(3) (Ru(1)—C(14) 2.114(4), Ru(3)—C(14) 2.159(5) Å) edges. The third edge Ru(2)—Ru(3) is bridged by the phosphido atom (P(2)) and the allylic group C(1)— Ru(3) is bridged by the phosphido atom (P(2)) and the allylic group C(1)—C(2)—C(3). The C(1)—C(2) and C(2)—C(3) bonds (1.390(7) and 1.421(7) Å, respectively) make an angle of 126.4(4)°; the angle between the C_3 and Ru_3 planes is 69.9(1)°. Atoms C(2), P(2), P(1) and Ru(1) define an approximate mirror plane that bisects the cluster normal to the Ru_3 triangle.

The terminal carbons of the allylic group C(1) and C(3) interact strongly with Ru(3) (2.197(6) Å) and Ru(2) (2.196(6) Å), respectively, while the central carbon atom is almost equidistant from these two metal atoms at a significantly greater separation (Ru(2)—C(2) 2.592(6), Ru(3)—C(2) 2.565(4) Å). A similar mode of attachment has been described in the complexes $Pd_2(\mu\text{-}I)(\mu\text{-}C_3H_5)(PPh_3)_2$ [6] and $Pd_2(\mu\text{-}C_3H_4Me\text{-}2)(\mu\text{-}C_5H_5)(L)_2$ (L = PPh_3, $P(OC_6H_4Me\text{-}2)_3$) [7] where the Pd-terminal carbon distances range from 2.10—2.20 Å, while the Pd-central carbon distances range from 2.50—2.56 Å.

Normally these central carbon-metal distances would be considered as too long for a bonding interaction, however, formal electron counting requires

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*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

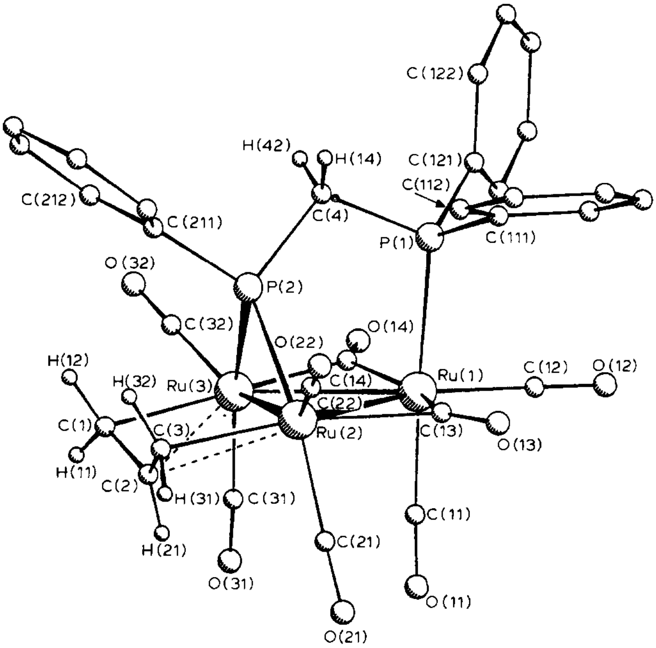

Fig. 1. PLUTO plot of the structure of $Ru_3(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_8$ (II), showing atom numbering scheme. Important bond distances and angles: Ru(1)—Ru(2) 2.853(1), Ru(1)—Ru(3) 2.853(1), Ru(2)—Ru(3) 2.887(1), Ru(1)—P(1) 2.411(1), Ru(2)—P(2) 2.359(1), Ru(3)—P(2) 2.344(1), P(1)—C(4) 1.827(5), P(2)—C(4) 1.835(4), Ru(1)—C(13) 2.079(4), Ru(2)—C(13) 2.185(5), Ru(1)—C(14), 2.114(4), Ru(3)—C(14) 2.159(5), Ru(2)—C(3) 2.196(6), Ru(2)—C(2) 2.592(6), Ru(3)—C(2) 2.565(4), Ru(3)—C(1) 2.197(6), C(1)—C(2) 1.390(7), C(2)—C93) 1.421(7) Å; Ru(1)—Ru(2)—Ru(3) 59.6(1), Ru(2)—Ru(3)—Ru(1) 59.6(1), Ru(3)—Ru(1)—Ru(2) 60.8(1), Ru(2)—P(2)—Ru(1) 75.7(1), Ru(3)—Ru(2)—C(3) 84.7(1),Ru(2)—Ru(3)—C(1) 85.5(1), Ru(2)—C(3)—C(2) 88.9(3), Ru(3)—C(1)—C(2) 88.3(4), Ru(3)—C(2)—Ru(2) 68.1(1), C(1)—C(2)—C(3) 126.4(4)°.

that the μ-C_3H_5 group is as acting a three-electron donor, indicating a weak π-interaction exists between the allyl group and the metal edge. MO calculations have shown that binuclear Pd complexes possess two acceptor orbitals (a_1 and b_1) which can overlap with the 1π and $2\pi_a$ orbitals of a μ-η^3-C_5H_5 ligand which coordinates to the metals in an analogous manner to II [8].

To our knowledge, no example of a μ-η^3-C_3H_5 group symmetrically attached to a metal cluster has been crystallographically characterised. Other cluster complexes containing allylic groups include $[PPh_4][Rh_6(\eta^3\text{-}C_3H_5)(CO)_{14}]$ [9], in which the C_3H_5 ligand is bonded to one metal atom only, and the well-known systems containing $2\eta^1,\eta^3$-C_3 ligands, such as $HRu_3(\mu_3\text{-}2\eta^1,\eta^3\text{-}CMeCHCEt)(CO)_9$ [10] or $HRu_3(\mu_3\text{-}2\eta^1,\eta^3\text{-}C_{12}H_{15})(CO)_9$ [11]. The trinuclear complexes $(\eta\text{-}C_5H_5)MM'Pt(\mu\text{-}CH_2CMeCH_2)(CO)_3(PPr^i_3)_2$ (M = Cr, Mo, W; M' = Pd, Pt) and $CoPd(\mu\text{-}CH_2CMeCH_2)(CO)_4(PPr^i_3)_2$ [12,13] also contain μ-allyl groups; however these have not yet been crystallographically characterised, so no structural comparison with II is possible.

Experimental

A solution of $Ru_3(CO)_{10}(dppm)$ (300 mg, 0.31 mmol) in THF (30 ml) was treated with $[K(HBBu^s_3)]$ (0.62 ml of a 0.5 mol l^{-1} solution in THF, 0.31 mmol).

After stirring at 25°C for 5 h the solvent was evaporated to dryness. Excess allyl chloride (2 ml) was added to the residue and the resulting mixture stirred for 10 min. The allyl chloride was removed under vacuum and the residue extracted with CH_2Cl_2 (ca. 5 ml). Filtration and addition of MeOH (ca. 5 ml) to the filtrate afforded golden yellow crystals of $Ru_3(\mu\text{-}\eta^3\text{-}C_3H_5)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_8$ (II) (88 mg, 32%), m.p. 169—171°C. (Found: C, 41.42; H, 2.21; $C_{30}H_{22}O_8P_2Ru_3$ calcd.: C, 41.15; H, 2.53%). Infrared (CH_2Cl_2): ν(CO) 2057s, 2018vs, 1983m, 1966m, 1857(br)m, 1813(br)m cm^{-1}.

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