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Preliminary communication

CARBON—HALOGEN BOND ACTIVATION AT $Ru_3(CO)_{12}$

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Summary

The structure of the complex $ClRu_3(CO)_9(C_2Ph)$, obtained by treating $Ru_3(CO)_{12}$ with $PhC{\equiv}CCl$, has been determined by X-ray methods. The three Ru and the Cl atoms are in a butterfly arrangement with the Ru—Ru hinge side open. The acetylide interacts through σ and π bonds with all three Ru atoms.

The reactions of alkynes and other unsaturated hydrocarbons with triruthenium and triosmium carbonyl clusters commonly involve oxidative addition with C—H cleavage. Following the cluster-surface analogy, this corresponds with dissociative chemisorption [1]. While carbon—halogen bond cleavage is the most common and important type of oxidative addition for mononuclear systems, this has hardly been studied at all for carbonyl clusters. As part of a detailed study of the reactions of carbonyl clusters with functionalised alkynes we have studied the cleavage of various types of bond. Recently we reported the cleavage of C—C bonds specifically adjacent to the triple bond in the reactions of $M_3(CO)_{12}$ (M = Ru or Os) with hydroxy- and dihydroxyalkynes not having α-hydrogen atoms [1,2]. For example, $HOCPh_2C{\equiv}CCPh_2OH$ gives $HM_3(CO)_9(C{\equiv}CPh_2OH)$. The phosphorus—carbon bond of $Ph_2PC{\equiv}CR$ is also cleaved in reactions with various metal carbonyls and $Ru_3(PPh_2)(CO)_9(C{\equiv}CR)$ is formed in this way [3].

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We now report that $Ru_3(CO)_{12}$ reacts readily with PhC≡CX (X = Cl or Br) to give moderate yields of the compounds $XRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-C≡CPh})$ [4] by C—X cleavage. There was no evidence for any products retaining the C—X bonds. This is probably the first example of a simple oxidative addition of a halocarbon at a trimetallic cluster. Very likely the ease of this reaction is related to the stability of the M_3(C≡CR) unit that is formed and on the ability of the μ_3-η^2 acetylide ligand in $XRu_3(CO)_9$(C≡CR) to accommodate a wide range of bridging groups X (hydride, halogen, PR_2, HgBr [5] or $AuPPh_3$ [6] or even the absence of such a ligand as in $[Ru_3(CO)_9(C≡CR)]^-$ [7]. In particular, it would seem that the μ_3-η^2-C_2R ligand can span both open and closed trimetallic clusters. To examine this aspect we determined the crystal structure of $ClRu_3(CO)_9(C_2Ph)$, even though the crystals were all of poor quality or twinned.

Crystal data: $C_{17}H_5ClO_9Ru_3$, M = 691.88, monoclinic space group $P2_1/n$, a 9.522(7), b 32.809(15), c 6.675(7) Å, β 93.11(5)°, V 2082(3) Å^3, D_c 2.207 g cm^{-3}, Z = 4. Full matrix least squares based on 1036 observed ($I \geqslant 2\sigma(I)$) of 3252 independent measured ($3 < \theta < 24°$) on a Siemens AED diffractometer using the Nb-filtered Mo-K_α radiation. Final R value: 0.109 [8].

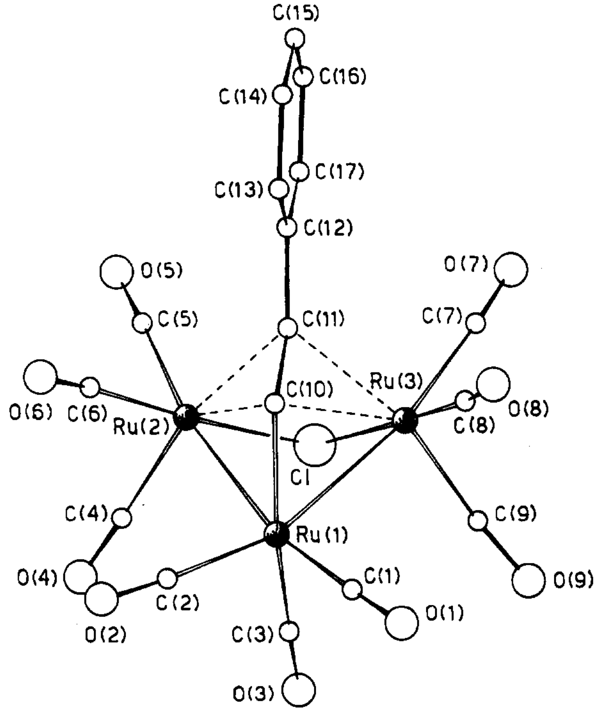

Fig. 1. View of the molecular structure of the complex $ClRu_3(CO)_9(C_2Ph)$ with the atomic numbering scheme. Selected bond distances (Å) and angles (°): Ru(1)—Ru(2) 2.815(5), Ru(1)—Ru(3) 2.805(5), Ru(2)—Cl 2.42(1), Ru(3)—Cl 2.46(2), Ru(1)—C(10) 1.95(2), Ru(2)—C(10) 2.25(2), Ru(2)—C(11) 2.32(2), Ru(3)—C(10) 2.30(2), Ru(3)—C(11) 2.28(2), C(10)—C(11) 1.29(3), Ru(2)—Ru(1)—Ru(3) 71.3(2), Ru(2)—Ru(1)—C(10) 52.7(5), Ru(3)—Ru(1)—C(10) 54.2(5), Ru(1)—Ru(2)—Cl 84.1(3), Ru(1)—Ru(3)—Cl 83.5(3), Ru(2)—Cl—Ru(3) 84.2(3).

The molecular structure of $ClRu_3(CO)_9(C_2Ph)$ is shown in Fig. 1 together with the most important bond parameters. The three Ru and the unique Cl atoms are in a butterfly arrangement (with the heteroatom on a wingtip) in which the "hinge" side is open (Ru(2)...Ru(3) 3.277(4) Å). The dihedral angle between the two triangle wings is 118°. Each Ru atom is bound to three terminal carbonyls and the acetylide C_2Ph ligand interacts with all the three Ru atoms via one σ-bond with Ru(1) and two π-bonds with Ru(2) and Ru(3).

In the $XRu_3(CO)_9(C_2R)$ complexes the length of the Ru(2)—Ru(3) side involved in the bridge is 2.792(3) when X = H [9], 2.900 when X = HgBr [5] and 2.820(1) Å when X = $AuPPh_3$ [6]; this side is considerably shortened when the hydride bridge is removed (2.665(3) Å in the anion [7]), in agreement with the increasing metal—metal bond. In the title complex the Cl bridge determines a remarkable lengthening of the bridged side, in agreement with the expected breaking of the metal—metal bond.

Apart from the variation of this length the $Ru_3(CO)_9(C_2R)$ framework remains practically unchanged in all the $XRu_3(CO)_9(C_2R)$ complexes, indicating a remarkable rigidity of this framework.

The ^{13}C NMR spectrum at −30°C of $ClRu_3(CO)_9(C_2Ph)$ (20% enriched with ^{13}CO) showed the expected five resonance (198.8(1), 198.2(2), 194.6(2), 190.4(2), 187.2(2) in ppm from internal TMS) consistent with the solid state structure and with a pattern very similar to those of $HRu_3(CO)_9(C_2R)$ and $[Ru_3(CO)_9(C_2R)]^-$. The coalescence temperature for CO exchange at the two equivalent Ru atoms are, however, very different: T_c −50°C (anion), +10°C (chloride) and +60°C (hydride). The ^{13}C chemical shifts are also in this order, and lower energy barriers seem to be related to higher electron densities at the metal atoms, although steric differences between these compounds may have some effect.

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References

1 S. Aime and A.J. Deeming, J. Chem. Soc. Dalton, (1981) 828.

2 S. Aime, L. Milone and A.J. Deeming, J. Chem. Soc. Chem. Commun., (1980) 1168.

3 A.J. Carty, S.A. MacLaughlin and N.J. Taylor, J. Organometal. Chem., 204 (1981) C27.

4 The reaction of $Ru_3(CO)_{12}$ (0.5 g) with PhC≡CCl (0.3 ml) in refluxing cyclohexane for 50 min gave a mixture which was separated by TLC (SiO_2; eluant, petroleum ether/diethyl ether 5/1 by volume) to give three yellow bands. The main band gave the product $ClRu_3(CO)_9(C_2Ph)$ (30%) as yellow crystals. ν(CO) in n-hexane: 2101w, 2080vs, 2058vs, 2030s, 2018vs, 1996w, 1990m cm^{-1}. The bromo compound prepared similarly but in slightly lower yield gave a very similar IR spectrum: 2099w, 2079vs, 2073sh, 2056vs, 2028s, 2017vs, 2003w, 1990m cm^{-1}.

5 R. Fahmy, K. King, E. Rosenberg, A. Tiripicchio and M. Tiripicchio Camellini, J. Amer. Chem. Soc., 102 (1980) 3626.

6 P. Braunstein, G. Predieri, A. Tiripicchio and E. Sappa, Inorg. Chim. Acta, 63 (1982) 113.

7 C. Barner-Thorsen, K.J. Hardcatle, E. Rosenberg, J. Siegel, A.M. Manotti Lanfredi, A. Tiripicchio and M. Tiripicchio Camellini, Inorg. Chem., 20 (1981) 4306.

8 Final atomic coordinates and thermal parameters are available from the authors on request.

9 M. Catti, G. Gervasio and S.A. Mason, J. Chem. Soc. Dalton, (1977) 2260.