Journal of Organometallic Chemistry, 279 (1985) C33—C36
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

ISOLATION OF THE MIXED-METAL CARBONYL CLUSTER ANION $[RuIr_3(CO)_9(\mu\text{-}CO)_3]^-$. CRYSTAL STRUCTURE OF ITS BIS(TRIPHENYLPHOSPHINE)IMINIUM SALT

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(Received September 18th, 1984)

Summary

The anion $[RuIr_3(CO)_{12}]^-$ has been isolated as one of the products from decomposition of $[RuIr_4(CO)_{15}]^{2-}$ in the absence of CO, and the structure of the bis(triphenylphosphine)iminium salt has been determined by X-ray diffraction. The anion is isoelectronic and isostructural with $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$, with the Ru atom located at one vertex of the metal triangle, which bears three edge-bridging carbonyls.

We previously reported that the pentanuclear dianion $[RuIr_4(CO)_{15}]^{2-}$ [1], like most of the 76 cluster valence electrons (CVE) trigonal bipyramidal clusters [2—5], is unstable in vacuum or in N_2, and decomposes predominantly to a brown mixed-metal cluster anion, which was isolated as the $[PPN]^+$ [6] salt, but not characterized. Further attempts to obtain this puzzling species in combination with various counter cations failed, but we were able to isolate another product of this process, $[RuIr_3(CO)_{12}]^-$. This new yellow anion was recovered from the mother liquor left by a fractional precipitation of the brown compound carried out by adding 2-propanol to a THF solution of the material obtained by subjection of $[PPN]_2[RuIr_4(CO)_{15}]$ to vacuum. Recrystallization from THF/hexane, gave yellow crystals of $[PPN][RuIr_3(CO)_{12}]$ suitable for X-ray crystallographic analysis. The IR spectrum of the product is shown in Fig. 1.

Crystal data. $C_{48}H_{30}Ir_3NO_{12}P_2Ru$, M = 1552.34, monoclinic, space group $P2_1/c$ (No. 14), a 14.988(2), b 20.009(2), c 16.685(2) Å, β 96.90(1)°, U 4968 Å^3,

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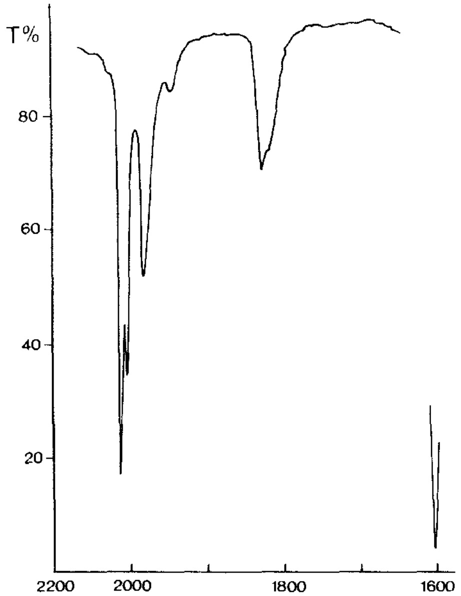

Fig. 1. IR spectrum of $[PPN][RuIr_3(CO)_{12}]$ in THF; bands (cm^{-1}) at 2050w, 2040s, 2002s, 1978ms, 1942w, 1823m, 1815sh (w = weak, s = strong, m = medium, sh = shoulder). Polystyrene (1601 cm^{-1}) was employed as a standard.

D_c 2.076 g cm^{-3}, $Z = 4$, $\mu(\text{Mo-}K_\alpha)$ 88.91 cm^{-1}. 8744 independent intensity data were collected on a Nonius CAD-4 automated diffractometer, within the 2θ sphere 6—50°. The structure was solved by Patterson and Fourier methods and refined by least-squares, using 5491 absorption-corrected reflections having $I \geqslant 3\sigma(I)$. The final values for R and R_w are 0.045 and 0.053, respectively*.

The anion $[RuIr_3(CO)_{12}]^-$ (Fig. 2) contains a tetrahedral cluster of metal atoms. The arrangement of ligands is similar to that in $Co_4(CO)_{12}$ [7] and $Rh_4(CO)_{12}$ [8], i.e. a basal metal atoms triangle bears three bridging and six terminal carbonyl ligands and an apical metal atom is bound to three terminal CO groups. $Ir_4(CO)_{12}$ shows a different ligands stereochemistry, the carbonyls being all terminal [9], but its derivatives containing ligands of poorer π-acidity, in place of one of the carbonyls prefer the $Rh_4(CO)_{12}$ stereochemistry [10,11], with the substituent bound to a metal of the CO-bridged triangle. The bridging carbonyl ligands in such compounds are involved in the charge equalization process, and thus it is not surprising to find the formally Ru^{1-} atom (which replaces an Ir atom in our compound) in the bridged basal triangle.

Within the metal framework, the Ir—Ir bond distances range from 2.707(1) to 2.728(1) Å, with a mean value of 2.715 Å, which can be compared with the mean value of 2.693 Å found in $Ir_4(CO)_{12}$ [9]. The Ru—Ir interactions are in the range 2.757(1)—2.787(1) Å, with a mean value of 2.770 Å. Because of the elongated trigonal bipyramidal geometry with the Ru atom in an apical position, the corresponding contacts in the cluster $[RuIr_4(CO)_{15}]^{2-}$ are much longer

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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.

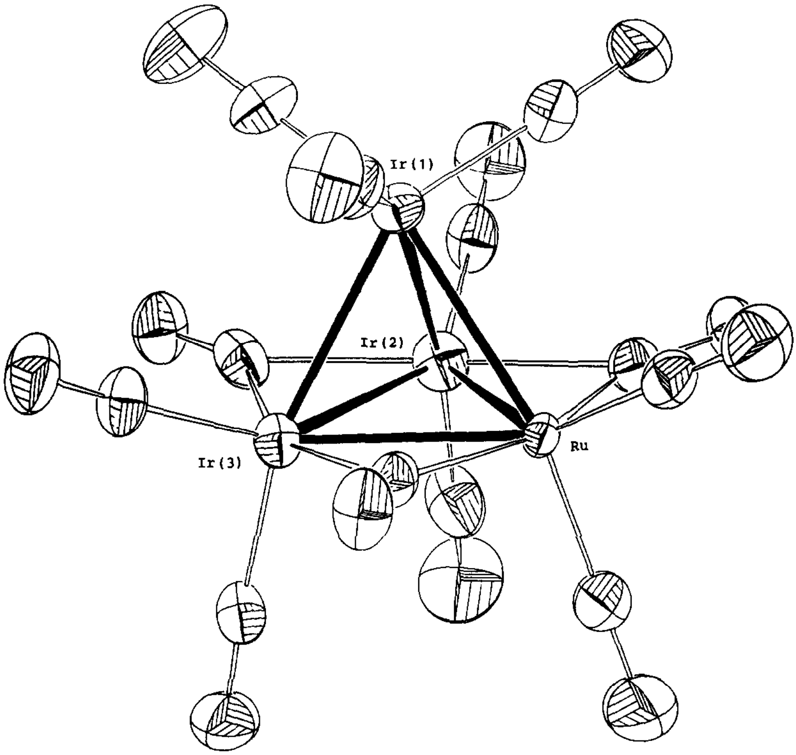

Fig. 2. ORTEP view of the $[RuIr_3(CO)_9(\mu\text{-}CO)_3]^-$ anion. The individual metal—metal bond lengths (Å) are: Ir(1)—Ir(2) 2.728(1), Ir(1)—Ir(3) 2.711(1), Ir(1)—Ru 2.766(1), Ir(2)—Ir(3) 2.707(1), Ir(2)—Ru 2.787(1), Ir(3)—Ru 2.757(1). The basal metal triangle is slightly disordered, the Ru atom being for the 10% in the Ir(2) position. The stereochemistry of the carbonyl ligands is however dictated by the shown metal arrangement.

(average value 3.01 Å). To our knowledge there is no other report of Ru—Ir bonding. Averaging of the mean Ir—Ir bond length in $Ir_4(CO)_{12}$ (2.693 Å) [9] and the mean Ru—Ru bond length in $Ru_3(CO)_{12}$ (2.854 Å) [12] gives a value of 2.773 Å in good agreement with that found in our compound.

The terminal CO ligands interact more strongly with the Ru atom (av. Ru—C 1.845 Å) than with Ir (av. Ir—C 1.900 Å), and this is particularly significant because the metal—metal bond lengths indicate a larger covalent radius for Ru than for Ir. This suggests that the anionic charge, formally located on the Ru atom, is mainly delocalized through the metal—ligand rather than metal—metal interactions.

The stereochemistry of the bridging carbonyls shared between the Ru and Ir atoms is influenced by the same factors. Such carbonyl ligands interact asymmetrically with the metals, the shorter bond lengths being towards the Ru atom (2.01 against 2.23 Å). The third bridging group between Ir(2) and Ir(3) is symmetrical (mean Ir—C 2.10 Å).

We are trying to develop a direct synthesis of this new tetranuclear mixed anion, and clarify the processes involved in the decomposition of $[RuIr_4(CO)_{15}]^{2-}$, which may help a better understanding of the peculiar chemistry of the pentanuclear clusters with 76 CVE.

References and notes

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