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Preliminary communication

SYNTHESIS AND STRUCTURE OF THE MIXED-METAL RUTHENIUM-COBALT ALKYNE CLUSTERS $NEt_4[RuCo_3(\mu\text{-}CO)_2(CO)_8(\mu_4\text{-}\eta^2\text{-}PhC{\equiv}CPh)]$ AND $RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}PhC{\equiv}CPh)$

PIERRE BRAUNSTEIN*, JACKY ROSE,

Laboratoire de Chimie de Coordination, ERA 670 CNRS, Institut Le Bel, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex (France)

and ODILE BARS

Laboratoire de Cristallochimie, LA 254 CNRS, Université de Rennes F-35042 Rennes Cedex (France)

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Summary

The tetrahedral cluster $NEt_4[RuCo_3(CO)_{12}]$ was prepared in 90% yield, and on treatment with excess $PhC{\equiv}CPh$ gave the "butterfly" cluster $NEt_4[RuCo_3(\mu\text{-}CO)_2(CO)_8(\mu_4\text{-}\eta^2\text{-}PhC{\equiv}CPh)]$. Reaction of the latter with HCl gave the neutral trimetallic cluster $RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}PhC{\equiv}CPh)$. Both products were characterized by single-crystal X-ray diffraction studies.

Reactions of mixed-metal ruthenium-cobalt clusters are of interest because of the significance of these metals in CO chemistry e.g. in catalysis of methanol homologation [1]. We recently reported the synthesis of $Na[RuCo_3(CO)_{12}]$ in 60—70% yield from $RuCl_3$(organonitrile)$_3$ and $NaCo(CO)_4$ [2]. This tetrametallic cluster was treated with Ph_3PAuCl to give the neutral cluster $Ph_3PAuRuCo_3(CO)_{12}$, which has a trigonal bipyramidal structure [2]. In order to evaluate the influence of the cation associated with $[RuCo_3(CO)_{12}]^-$ on its chemistry, we have now prepared $NEt_4[RuCo_3(CO)_{12}]$ (I) which was obtained in ca. 90% yield, from $NEt_4[RuCl_4(CH_3CN)_2]$ [3], according to the reaction:

$$NEt_4[RuCl_4(CH_3CN)_2] + 3\ Co_2(CO)_8 \xrightarrow[5\ h,\ 50^\circ C]{THF} NEt_4[RuCo_3(CO)_{12}] + \ldots \quad (1)$$

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Complex I does not react with Ph_3PAuCl under conditions in which $Na[RuCo_3(CO)_{12}]$ reacts. However, it reacts with C_2Ph_2 (acetone, reflux) to afford $NEt_4[RuCo_3(CO)_{10}C_2Ph_2]$ (II, 75% yield), whereas under similar conditions the corresponding sodium salt could not be isolated. The nature of the cation (small cations enhance the activity of nucleophilic anions) thus has opposite effects in reactions of $[RuCo_3(CO)_{12}]^-$ with electrophiles or nucleophiles. The infrared spectrum of II exhibits ν(CO) (KBr) bands at 2050s, 2015s, 1983vs, 1958vs, 1900m, 1837sh, 1825s, 1799s cm^{-1}. The visible spectrum shows an absorption at $\lambda_{max}(CH_2Cl_2)$ 522 nm.

Crystals of II suitable for X-ray diffraction were obtained from acetone/hexane.

Crystal data for II. $C_{32}H_{30}NCo_3O_{10}Ru$, M = 866, triclinic, space group $P\bar{1}$, a 11.46(5), b 16.79(4), c 20.26(6) Å, α 110.0(2), β 95.6(3), γ 93.4(3)°, U 3627 Å^3, Z = 4, D_c 1.587 g cm^{-3}, $F(000)$ = 1736, μ(Mo-K_α) 17.9 cm^{-1}. Current R = 0.072 (R_w = 0.088) for 4219 unique reflections ($I \geqslant 3\sigma(I)$) measured on an Enraf—Nonius CAD4 diffractometer ($4 \leqslant 2\theta \leqslant 44°$). The structure was solved by direct methods (MULTAN) and by successive Fourier differences,

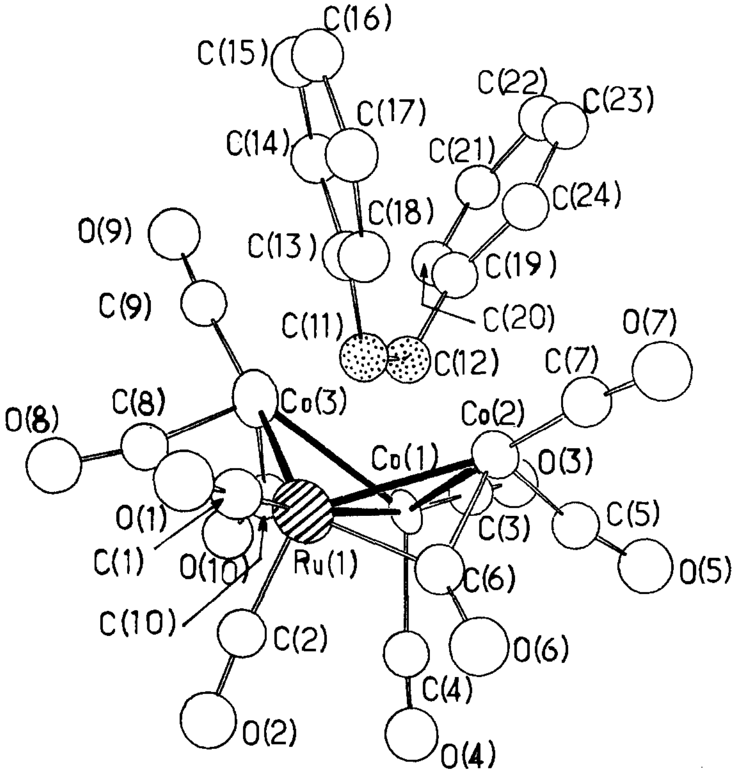

Fig. 1. Diagram of the molecular structure of one molecule of $NEt_4[RuCo_3(\mu\text{-}CO)_2(CO)_8\text{-}(\mu_4\text{-}\eta^2\text{-}C_2Ph_2]$ (II) (see text). The cation has been omitted for clarity. Principal dimensions are: Ru(1)—Co(1) 2.725(2); Ru(1)—Co(2) 2.525(2); Ru(1)—Co(3) 2.493(2); Co(1)—Co(2) 2.481(2); Co(1)—Co(3) 2.518(2); Co(2). . .Co(3) 3.549(2); Ru(1)—C(6) 1.94(1); Co(2)—C(6) 1.83(1); Ru(1)—C(11) 2.13(1); Co(2)—C(11) 2.07(1); Co(3)—C(11) 2.12(1); Co(1)—C(12) 2.14(1); Co(2)—C(12) 2.14(1); Co(3)—C(12) 2.06(1); C(11)—C(12) 1.34(1) Å.

and refined by full matrix least-squares using PDP 11, SDP(2) calculation system, with Ru, Co atoms anisotropic, C, N, O atoms isotropic, H atoms were introduced at the calculated positions. Two independant molecules were found in the unit cell but these differ only slightly in the orientation of the ligands, and so we describe only one of them*.

The molecular structure of $NEt_4[RuCo_3(\mu\text{-}CO)_2(CO)_8(\mu_4\text{-}\eta^2\text{-}PhC{\equiv}CPh)]$ is shown in Fig. 1, together with some important bond parameters. The ruthenium atom occupies a hinge position in the $RuCo_3$ "butterfly". The angle between the normals to the RuCo(1)Co(2) and RuCo(1)Co(3) wings is 64.8°. Ru(1) and Co(1) are bonded to two terminal carbonyls, two bridging CO ligands span the Ru(1)—Co(2) and Co(1)—Co(3) edges whereas C(5)O(5) and C(8)O(8) are semi-bridging between Co(1)—Co(2) and Ru(1)—Co(3). The Ru(1)—Co(1) hinge bond is significantly longer than any other metal—metal bond in the molecule. This resembles the situation found in $Fe_4(CO)_{12}(COOCH_3)^-$, another 60 electron cluster having a *closo* trigonal bipyramidal structure with six electron pairs [4]. Cluster II is best described as a 6 skeletal atoms $RuCo_3C_2$ *closo*-octahedron with 7 skeletal electron pairs [5]. The $\mu_4\text{-}\eta^2\text{-}C_2Ph_2$ ligand lies above the $RuCo_3$ butterfly completing the $RuCo_3C_2$ distorted octahedron. Upon π-coordination to Co(2) and Co(3), the acetylenic triple bond is lengthened by 0.14 Å compared to the free ligand (1.198(3) Å [6]). The occurrence of the reaction leading to II may explain the formation of the recently described $RuCo_3(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}Bu^tC{\equiv}CH)(\mu\text{-}CO)_2(CO)_7$ cluster [7].

Interestingly, cyclic voltammetry of II on a Pt electrode shows a reversible reduction ($E_{1/2}$ −1.28 V vs. SCE in 1,2-$C_2H_4Cl_2$ and 0.1 *M* $(n\text{-}C_6H_{13})_4NClO_4$), whereas I is irreversibly reduced under similar conditions [8].

Reaction of II with HCl in H_2O/acetone occurs with change of colour from violet to red. Extraction with hexane gives a neutral complex in 20% yield. This complex III has infrared absorptions in the ν(CO) region (KBr) at: 2096m, 2062vs, 2049vs, 2035s, 2021s, 1998s, 1981s, 1877s cm^{-1}. This complex was obtained as red crystals from hexane, and characterized as $RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}PhC{\equiv}CPh)$ by X-ray analysis.

Crystal data: $C_{23}H_{10}Co_2O_9Ru$, $M = 649$, monoclinic, space group $P2_1/n$, a 8.687(3), b 23.57(1), c 11.759(7) Å, β 96.83(4)°, U 2390 Å^3, $Z = 4$, D_c 1.8 g cm^{-3}, $F(000) = 1276$, $\mu(Mo\text{-}K_\alpha)$ 20.3 cm^{-1}. Current $R = 0.043$ ($R_W = 0.052$) for 4048 unique reflections ($I \geqslant 3\sigma(I)$). The structure was solved and refined using the same methods as for II, except for the atomic coordinates of the H atoms which were refined.

The molecular structure of III is illustrated in Fig. 2, together with some important bond parameters.

This 48 electron cluster consists of a triangular array of two Co and one Ru atoms. The only non linear CO ligand is C(9)O(9) which is semi-bridging between Ru and Co(2) (Co(2)—C(9)—O(9) 149.9(1)°, Co(2)—Co(9) 1.820(3), Ru. . .C(9) 2.284(3) Å). The C_2Ph_2 ligand interacts with all three metal atoms

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

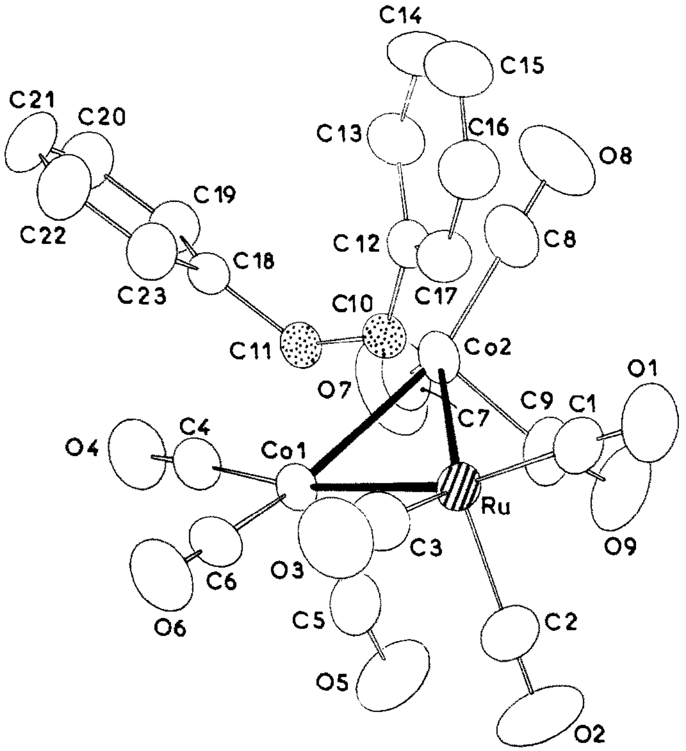
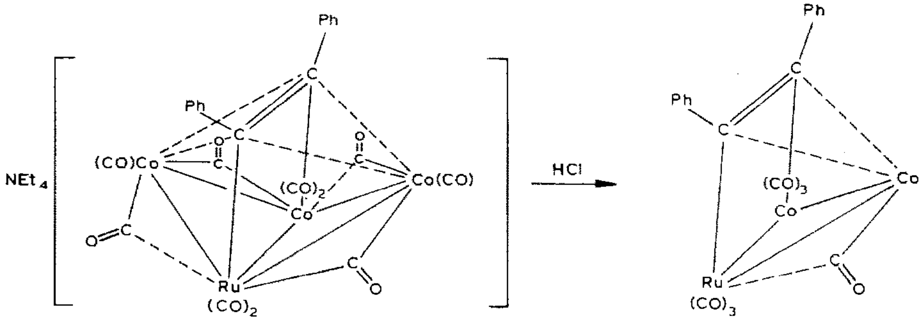


Fig. 2. Diagram of the molecular structure of $RuCo_2(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2Ph_2)$ (III). Principal dimensions are: Ru—Co(1) 2.6875(5); Ru—Co(2) 2.5865(5); Co(1)—Co(2) 2.4535(5); Ru—C(10) 2.124(2); Co(1)—C(11) 1.976(2); Co(2)—C(10) 2.080(2); Co(2)—C(11) 2.072(2); C(10)—C(11) 1.370(3) Å.

and is nearly parallel to the Ru—Co(1) edge of the cluster. The $\mu_3(\eta^2\text{-}\|)$ bonding mode of the alkyne is in agreement with the *nido*-octahedral structure of III, expected for this 7 skeletal electron pairs cluster [5]. This situation has so far been encountered in about ten mixed-metal clusters [9]. Noteworthy, in the related $FeCo_2(CO)_9C_2Et_2$ cluster [10], the alkyne is also bonded in a $\mu_3(\eta^2\text{-}\|)$ mode but in contrast with III, it is parallel to the Co—Co vector.

Clearly, III has kept the "memory" of its precursor and can be formally deduced from II by removal of the $[Co(3)(CO)]^-$ fragment.



(II)

(III)

The molecular reorganization induced by the "protonation" of II illustrates the possible role of the alkyne ligand in maintaining the cohesion of a trimetallic $RuCo_2$ face.

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References

1 M.E. Fakley and R.A. Head, Applied Catal. 5 (1983) 3; Rhone-Poulenc, Eur. Patent 22 038 (1979); Gulf Co., Eur. Patent 13464 (1980).
2 P. Braunstein, J. Rosé, Y. Dusausoy and J.P. Mangeot, C.R. Acad. Sci. Paris, 294 (1982) 967.
3 J. Dehand and J. Rosé, Inorg. Chim. Acta, 37 (1979) 249.
4 J.S. Bradley, G.B. Answell, M.E. Leonowicz and E.W. Hill, J. Am. Chem. Soc., 103 (1981) 4968.
5 K. Wade, Adv. Inorg. Chem. Radiochem., 18 (1976) 67.
6 A. Mavradis and J. Moustakali-Mavradis, Acta Cryst. B, 33 (1977) 3612.
7 D.F. Jones, P.H. Dixneuf, A. Benoit and J.Y. Le Marouille, J. Chem. Soc., Chem. Commun., (1982) 1217.
8 P. Lemoine, private communication.
9 E. Sappa, A. Tiripicchio and P. Braunstein, Chem. Rev., in press.
10 S. Aime, L. Milone, D. Osella, A. Tiripicchio and A.M. Manotti-Lanfredi, Inorg. Chem., 21 (1982) 501.