

Reactivity of $[\text{Ru}_3(\mu\text{-H})(\mu\text{-Me}_2\text{pz})(\text{CO})_{10}]$ with 2,4-hexadiyne. Characterization of the first tetranuclear ynenyl complex

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Abstract

The tetranuclear ynenyl complex $[\text{Ru}_4(\mu\text{-}\eta^2\text{-Me}_2\text{pz})(\mu_4\text{-}\eta^4\text{-MeCH=C-C}\equiv\text{CMe})(\mu\text{-CO})(\text{CO})_{10}]$ (Me_2pz = 3,5-dimethylpyrazolate) has been prepared by reaction of $[\text{Ru}_3(\mu\text{-H})(\mu\text{-}\eta^2\text{-Me}_2\text{pz})(\text{CO})_{10}]$ with 2,4-hexadiyne and has been characterized by X-ray diffraction methods. It consists of an unusual broken-wing butterfly (spiked triangle) tetraruthenium framework (64-electron) with all the metal atoms bridged by a hex-2-yn-4-en-4-yl ligand (7-electron donor). This type of coordination is unprecedented for ynenyl ligands. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Although the first reports mentioning the pyrazolate-bridged triruthenium cluster $[\text{Ru}_3(\mu\text{-H})(\mu\text{-}\eta^2\text{-Me}_2\text{pz})(\text{CO})_{10}]$ (**1**) (Me_2pz = 3,5-dimethylpyrazolate) are rather old [1–3], reactivity studies on it could only be conveniently undertaken a few years ago when a high-yield preparation was achieved [4]. This preparation involves the sequential treatment of $[\text{Ru}_3(\mu\text{-H})(\mu\text{-CO})(\text{CO})_{10}]^-$ with 3,5-dimethylpyrazole and trifluoroacetic acid [4]. The previously reported thermal reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with 3,5-dimethylpyrazole only gives low yields of complex **1** [1,2] and binuclear ruthenium(I) derivatives [2,3]. As part of a general study of the reactivity of compound **1** [4,5], we decided to investigate the reactions of **1** with diynes.

Diynes have recently started to attract the attention of organometallic cluster chemists [6–12] because they are more reactive and are expected to lead to a richer, though more complicated, derivative chemistry than monoalkynes.

Interestingly, only two ynenyl derivatives have so far been reported as products of reactions of carbonyl metal clusters with diynes, namely, the ruthenium derivatives $[\text{Ru}_3(\mu_3\text{-pyNMe})(\mu\text{-}\eta^3\text{-PhCH=C-C}\equiv\text{CPh})(\mu\text{-CO})_2(\text{CO})_6]$ [9] and $[\text{Ru}_2(\mu\text{-N=CPh}_2)(\mu\text{-}\eta^2\text{-CH}_2\text{=CCH}_2\text{C}\equiv\text{CSiMe}_3)(\text{CO})_6]$ [10], which arise from the insertion of diynes into a metal-hydride bond of trinuclear cluster precursors. The osmium derivatives $[\text{Os}_3(\mu\text{-H})(\mu_3\text{-}\eta^3\text{-E-FcCH=C-C}\equiv\text{CFc})(\text{CO})_9]$ (Fc = ferrocenyl), $[\text{Os}_3(\mu\text{-OH})(\mu_3\text{-}\eta^3\text{-Z-FcCH=C-C}\equiv\text{CFc})(\text{CO})_9]$, $[\text{Os}_3(\mu\text{-OH})(\mu_3\text{-}\eta^3\text{-E-FcCH=C-C}\equiv\text{CFc})(\text{CO})_9]$ are formed in the reaction of $[\text{Os}_3(\mu_3\text{-}\eta^2\text{-FcC}\equiv\text{C-C}\equiv\text{CFc})(\text{CO})_{10}]$ [6a] with water [6b]. It should be noted that the ynenyl ligands of the first two complexes are attached to two metal atoms, while those of the osmium compounds are attached to three metal atoms. An additional cluster complex with an ynenyl ligand attached to three metal atoms has been reported, $[\text{Ru}_3\{\mu\text{-NS(OMePh)}(\mu\text{-}\eta^3\text{-PhCH=C-C}\equiv\text{CPh})(\text{CO})_9]$, but in this case the ynenyl ligand arises from the coupling of two monoalkyne fragments [13].

We now report the preparation and full characterization of the first complex in which an ynenyl ligand is attached to four metal atoms. This complex results from the thermal reaction of compound **1** with 2,4-hexadiyne.

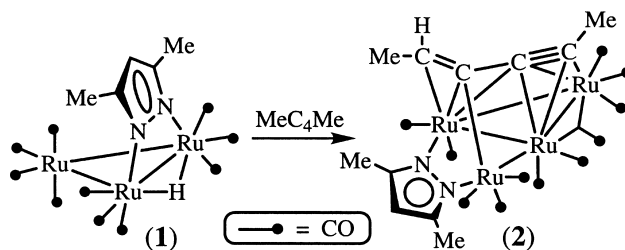
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2. Results and discussion

The reaction of complex **1** with 2,4-hexadiyne in THF at reflux temperature gave a mixture of compounds from which the tetranuclear ynenyl derivative $[\text{Ru}_4(\mu\text{-}\eta^2\text{-Me}_2\text{pz})(\mu_4\text{-}\eta^4\text{-MeCH=C-C}\equiv\text{CMe})(\mu\text{-CO})_{10}]$ (**2**) was separated by chromatographic methods and isolated in 26% yield (Scheme 1).¹

The tetranuclear nature of **2** was pointed out by its FAB MS, which shows the peaks corresponding to the molecular ion isotopomers. The presence of an ynenyl ligand with a hydrogen atom adjacent to a methyl group was also suggested by its ¹H NMR spectrum which, in addition to four singlet resonances (three for the pyrazolate protons and one for a methyl group of the ynenyl ligand), it shows a CH proton (quartet) coupled ($J = 6.0$ Hz) to a methyl group (doublet).

The molecular structure of this complex was determined by X-ray diffraction methods (Fig. 1).² Selected interatomic distances are given in the legend of Fig. 1. The metallic framework of the complex can be described as a broken-wing butterfly (spiked triangle) arrangement of four ruthenium atoms, since the Ru(1)–Ru(4) distance, 3.387(1) Å, is too long to be considered as a metal–metal bond. Such a metal arrangement, although common for osmium clusters, is rare for ruthenium derivatives [14]. A hex-2-yn-4-en-4-yl ligand is attached to



Scheme 1.

all the metal atoms. The alkyne fragment, C(1e)–C(1d), of this ligand interacts with the metal triangle in a distorted μ_3 -perpendicular arrangement. This distortion seems to be imposed by the coordination of the alkene fragment, C(1b)–C(1c), of the ynenyl ligand to one of the atoms of the metallic triangle, Ru(4). The spiked metal atom, Ru(1), is σ -bonded to the internal carbon atom, C(1c), of the alkene fragment. The C–C distance of the coordinated triple bond is 1.34(1) Å, while that of the coordinated double bond is 1.38(1) Å. The neighboring C–C bond, C(1c)–C(1d), is formally single, but its C–C distance is rather short, 1.40(1) Å, indicating some multiple-bond character. The pyrazolate ligand spans the ruthenium atoms of the broke-wing part of the metallic core. The cluster shell is completed by one semibridging, C(32)–O(32), and 10 terminal carbonyl ligands.

¹ 2,4-Hexadiyne (23 mg, 0.282 mmol) was added to a solution of compound **1** (150 mg, 0.221 mmol) in THF (20 ml). The solution was heated at reflux temperature for 1 h. The solvent was removed under reduced pressure. The residue was dissolved in a minimal amount of dichloromethane and the solution was separated by TLC (silica gel) using hexane as eluant. The first band, yellow, afforded a mixture of unidentified compounds. The second band, orange, gave compound **2** (51 mg, 26% based on the amount of initial Me_2pz). Calcd. for $\text{C}_{22}\text{H}_{14}\text{N}_2\text{O}_{11}\text{Ru}_4$ ($M = 886.63$): C, 29.80; H, 1.59; N, 3.16. Found: C, 29.86; H, 1.65; N, 3.12. FABMS (m/z): 888 [M^+]. IR ν_{CO} (cm^{-1} in hexane): 2088 (w), 2067 (vs), 2026 (s), 2011 (s), 1996 (sh), 1974 (sh), 1950 (w), 1900 (w), 1780 (w), ¹H NMR (δ in CDCl_3): 5.63 (s, 1 H), 5.25 (q, $J = 6.0$ Hz, 1 H), 2.58 (s, 3 H), 2.22 (s, 3 H), 2.10 (s, 3 H), 1.84 (d, $J = 6.0$ Hz, 3 H).

² Crystal data and details of refinement are as follows: $\text{C}_{22}\text{H}_{14}\text{N}_2\text{O}_{11}\text{Ru}_4$; $fw = 886.63$; cryst. size = $0.5 \times 0.3 \times 0.3$ mm³; cryst. system = monoclinic; space group = $C2/c$; $a = 27.658$ (6) Å; $b = 13.345$ (3) Å; $c = 17.126$ (3) Å; $\beta = 121.74$ (3); $V = 5376$ (1) Å³; $Z = 8$; $\rho_{\text{calcd.}} = 2.191$ g/cm³; $\mu = 2.265$ mm⁻¹; radiation = Mo K α ; $\lambda = 0.71073$ Å; $F(000) = 3392$; index range: $-32 > h < 27$, $-15 < k < 0$, $0 < l < 20$; $2\theta = 49.94^\circ$; temp = 293 (2) K; collected refl. = 4888; unique refl. = 4713; observed refl. ($F < 4\sigma(F)$) = 3055; $R_{\text{int}} = 0.0398$; no. of variables = 352; weighting scheme = $w^{-1} = \sigma^2 F_0^2 + (0.0513P)^2 + 21.79740P$, $P = (F_0^2 + 2F_c^2)/3$; GoF = 0.984; final $R_{(4\sigma)} = 0.0402$; final $wR_{2(\text{all data})} = 0.1128$; large res. peak = 1.072 e/Å. Crystallographic data for compound **2** have been deposited with the Cambridge Crystallographic Data Centre with the depositor number CCDC-150161. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk, or http://www.ccdc.cam.ac.uk).

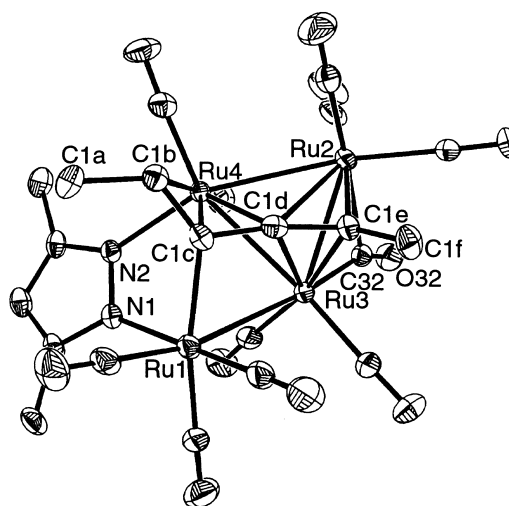


Fig. 1. Molecular structure of compound **2**. Selected interatomic distances (Å): Ru(1)–Ru(3) 2.904 (1), Ru(1)–Ru(4) 3.387 (1), Ru(2)–Ru(3) 2.781 (1), Ru(2)–Ru(4) 2.846 (1), Ru(3)–Ru(4) 2.818 (1), Ru(1)–N(1) 2.125 (7), Ru(4)–N(2) 2.107 (7), Ru(1)–C(1c) 2.118 (9), Ru(2)–C(1d) 2.530 (9), Ru(2)–C(1e) 2.225 (9), Ru(3)–C(1d) 2.195 (8), Ru(3)–C(1e) 2.225 (9), Ru(4)–C(1b) 2.375 (9), Ru(4)–C(1c) 2.232 (8), Ru(4)–C(1d) 2.223 (8), Ru(2)–C(32) 2.44 (1), Ru(3)–C(32) 1.96 (1), mean Ru–C_{(CO)terminal} 1.91 (1), C(32)–O(32) 1.15 (1), mean C–O_{(CO)terminal} 1.12 (1), C(1a)–C(1b) 1.51 (1), C(1b)–C(1c) 1.38 (1), C(1c)–C(1d) 1.40 (1), C(1d)–C(1e), 1.34 (1), C(1e)–C(1f) 1.49 (1).

The reactions of compound **1** with other diynes, such as diphenylbutadiyne and 1,6-diphenoxy-2,4-hexadiyne, were also investigated. Unfortunately, they led to complicated mixtures of compounds that could not be successfully separated. A similar situation was encountered when the reactivity of compound **1** with monoalkynes was studied [5b].

In conclusion, the results reported herein demonstrate that conjugated ynenyl ligands can coordinate to four metal atoms, a situation that appears to be heretofore unprecedented.

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