

NiRu₄(CO)₉(μ-PPh₂)₂(μ₄-C≡CPrⁱ)₂ : A Pentanuclear Mixed Metal Cluster with a Novel Metal Framework

Maurizio Lanfranchi,^a Antonio Tiripicchio,^a Enrico Sappa,^b Shane A. MacLaughlin,^c and Arthur J. Carty^c

^a *Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffattometrica del C.N.R., Via M. D'Azeglio 85, 43100 Parma, Italy*

^b *Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso M. D'Azeglio 48, 10125 Torino, Italy*

^c *Guelph-Waterloo Centre, Waterloo Campus, Chemistry Department, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*

The synthesis of a novel pentanuclear nickel–ruthenium cluster, [NiRu₄(CO)₉(μ-PPh₂)₂(μ₄-C≡CPrⁱ)₂], via the addition of an electron-rich species [(η-C₅H₅)Ni(CO)]₂ to a carbocationic μ₃-acetylide group in [Ru₃(CO)₉(μ₃-C≡CPrⁱ)(PPh₂)] is described; the X-ray structural analysis has shown that the metal framework consists of a ruthenium atom butterfly with the open edge bridged by a nickel atom, and the two acetylide ligands are co-ordinated in multi-site fashion to the metal cluster.

In seeking to exploit the demonstrated carbocationic character of multi-site bound acetylide ligands¹ we have treated the cluster [Ru₃(CO)₉(μ₃-η²-C≡CPrⁱ)(PPh₂)] with the electron-rich species [(η-C₅H₅)Ni(CO)]₂ with the aim of generating mixed polynuclear metal compounds. We describe herein the synthesis and X-ray structural analysis of a pentanuclear mixed metal cluster [NiRu₄(CO)₉(μ-PPh₂)₂(μ₄-C≡CPrⁱ)₂] (**1**) which has a novel hetero-metallic framework consisting of a Ru₄ butterfly 'zipped up' by a Ni(CO) group. Of the known pentanuclear clusters the most common skeletal arrangements are square pyramidal and trigonal bipyramidal^{2,3} although recently examples of other triangulated structures⁴ have appeared. A further interesting feature of (**1**) is the uncommon μ₄-η²-bonding of the two acetylide groups to the heterometallic cluster.

Reaction of [Ru₃(CO)₉(μ₃-η²-C≡CPrⁱ)(PPh₂)]⁵ (1 mmol) with [(η-C₅H₅)Ni(CO)]₂ (2 mmol) in heptane under reflux (30 min) afforded four products, as indicated by t.l.c. and i.r. monitoring. Complex (**1**) [ν_{CO} (CCl₄) 2076w, 2058m sh, 2030s, 2003vs, 1981vs, and 1970m] has been fully characterized by X-ray diffraction methods. Black crystals of (**1**) were obtained by slowly cooling the heptane solution under nitrogen; these decompose indistinctly in the range 100–140 °C. Attempts to sublime (**1**) under high vacuum in the introduction systems of the mass spectrometer resulted in total decomposition. The registration of good ¹H n.m.r. spectra was prevented by partial

decomposition of paramagnetic products during the analysis. The elemental analysis was in satisfactory agreement with the molecular formulation of (**1**).

Crystal data: C₄₃H₃₄NiO₉P₂Ru₄.1/2C₂H₆O, *M* = 1242.71, monoclinic, space group *P*2₁/*c*, *a* = 15.008(9), *b* = 15.311(11), *c* = 21.108(14) Å, β = 98.92(8)°, *U* = 4792(6) Å³, *Z* = 4, *D*_c = 1.72 g cm⁻³; *F*(000) = 2444, μ(Mo-K_α) = 17.13 cm⁻¹. The intensities of 7542 independent reflections were collected on a Siemens AED diffractometer (with θ in the range 3–24°), using Nb-filtered Mo-K_α radiation and the θ–2θ scan technique. The structure was solved by combined direct and Patterson methods and refined by full-matrix least-squares on the basis of 2789 observed reflections [having *I* ≥ 2σ(*I*)] to an *R*-value of 7.4%.†

Both terminal isopropyl groups are disordered over two positions of nearly equivalent occupancy. In the preliminary stages of the structure determination one of the two isopropyl groups seemed to be an isopropenyl group. The final difference Fourier map revealed the presence of an unexpected disordered triatomic molecule, which was interpreted as ethanol.

† The atomic co-ordinates for this work 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.

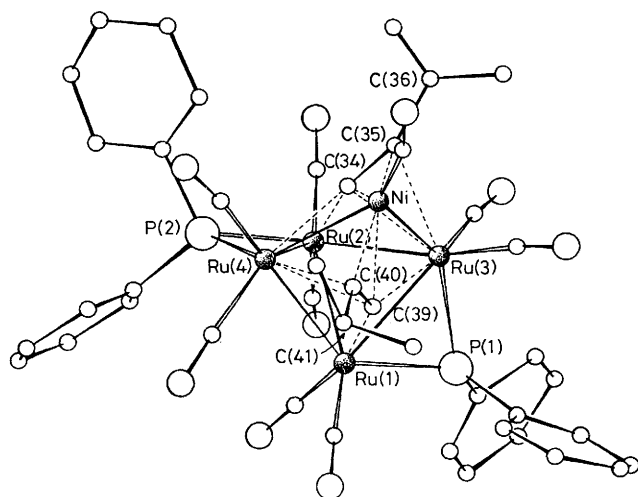


Figure 1. A view of the molecular structure of the complex (1). Important bond lengths: Ru(1)–Ru(2) 2.813(5), Ru(1)–Ru(3) 2.771(5), Ru(1)–Ru(4) 2.789(8), Ru(2)–Ru(3) 2.831(5), Ru(2)–Ru(4) 2.770(4), Ru(3)–Ni 2.662(6), Ru(4)–Ni 2.668(6), Ru(1)–P(1) 2.230(9), Ru(3)–P(1) 2.287(9), Ru(2)–P(2) 2.256(9), Ru(4)–P(2) 2.291(9), Ru(1)–C(39) 2.04(3), Ru(2)–C(34) 2.06(2), Ru(3)–C(34) 2.25(2), Ru(3)–C(35) 2.44(3), Ru(3)–C(39) 2.27(4), Ru(4)–C(34) 2.31(2), Ru(4)–C(39) 2.28(3), Ru(4)–C(40) 2.50(3), Ni–C(34) 2.02(2), Ni–C(35) 1.99(3), Ni–C(39) 2.08(4), Ni–C(40) 1.89(3), C(34)–C(35), 1.34(3), and C(39)–C(40) 1.38(4) Å.

The structure of the complex (1) is shown in Figure 1, and the more significant bond distances are given. The pentanuclear metal framework consists of a tetraruthenium 'butterfly' with a nickel atom symmetrically bridging the open edge Ru(3)–Ru(4) [3.568(6) Å]. Because of this bridge, the dihedral angle between the triangular wings Ru(1)–Ru(2)–Ru(3) and Ru(1)–Ru(2)–Ru(4) is rather narrow, 95.6(6)°, if compared with other Ru butterfly clusters. Two edges, Ru(1)–Ru(3) and Ru(2)–Ru(4), are bridged by phosphido-groups. Of nine carbonyl ligands eight are terminally bound to Ru atoms (two for each metal) and one, bound to the Ni atom, is bent [Ni–C(9)–O(9) 162°] probably owing to steric hindrance involving C(35) and C(40) of the acetylide groups. The acetylide ligands are co-ordinated in multi-site fashion with the α -carbon atoms C(34) and C(39) bound to four metal atoms Ru(2), Ru(4), Ni, and Ru(3), and to Ru(1), Ru(3), Ni, and Ru(4), respectively, and the β -atoms C(35) and C(40) co-ordinated to Ni and Ru(3), and to Ni and Ru(4), respectively. Only one other example of this μ_4 - η^2 -acetylide bonding, in the homonuclear cluster [Ru₅(CO)₁₃(PPh₂)(C≡CPh)],⁶ is known to us. The complex (1) presents an approximate C₂ symmetry as shown by Figure 2.

The location of the α -carbon atoms of the acetylide ligands with respect to the metal atoms in (1) does however bear a strong resemblance to the carbidic carbon atoms in butterfly cluster carbides⁷ where unusual carbocationic reactivity is associated with the multi-site bonding mode.

The loss of a cyclopentadienyl group from the $[(\eta\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})_2]$ precursor with retention of a CO ligand in the synthesis of (1) is highly unusual. Indeed the synthesis of a wide variety of nickel-iron,⁸ nickel-ruthenium,⁹ and nickel-osmium¹⁰ clusters using this reagent as a source of nickel results predominantly in the incorporation of $(\eta\text{-C}_5\text{H}_5)\text{Ni}$ units into the mixed clusters.

There is now accumulating evidence that multi-site bound acetylides,^{1,11} like their carbide counterparts,⁷ are exceedingly electrophilic. Addition of nucleophiles including electron-rich

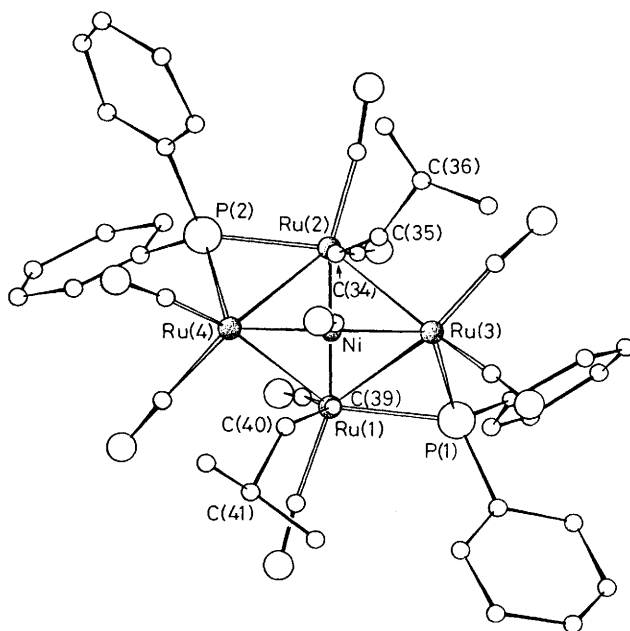


Figure 2. View of the complex showing the approximate C₂ symmetry.

transition metal fragments is a potentially powerful method for elaboration of these molecules and for the synthesis of high nuclearity clusters.

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References

- 1 Y. S. Wong, H. N. Paik, P. C. Chieh, and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 1975, 309; A. J. Carty, G. N. Mott, N. J. Taylor, and J. E. Yule, *J. Am. Chem. Soc.*, 1978, **100**, 3051; A. J. Carty, G. N. Mott, and N. J. Taylor, *J. Organomet. Chem.*, 1981, **212**, C54; A. J. Carty, *ACS Adv. Chem. Ser.* 1981, in the press.
- 2 W. L. Gladfelter and G. L. Geoffroy, *Adv. Organomet. Chem.*, 1980, **18**, 207.
- 3 B. F. G. Johnson and J. Lewis, *Adv. Inorg. Chem. Radiochem.*, 1981, **24**, 225.
- 4 D. H. Farrar, B. F. G. Johnson, J. Lewis, J. N. Nicholls, P. R. Raithby, and M. J. Rosales, *J. Chem. Soc., Chem. Commun.*, 1981, 273.
- 5 A. J. Carty, S. A. MacLaughlin, and N. J. Taylor, *J. Organomet. Chem.*, 1981, **204**, C27.
- 6 A. J. Carty, S. A. MacLaughlin, and N. J. Taylor, *J. Am. Chem. Soc.*, 1981, **103**, 2456.
- 7 J. S. Bradley, G. B. Ansell, and W. E. Hill, *J. Am. Chem. Soc.*, 1979, **101**, 7417; M. Tachikawa and E. L. Muetterties, *J. Am. Chem. Soc.*, 1980, **102**, 4541.
- 8 E. Sappa, A. Tiripicchio, and M. Tiripicchio Camellini, *J. Organomet. Chem.*, 1980, **199**, 243.
- 9 E. Sappa, A. Tiripicchio, and M. Tiripicchio Camellini, *J. Organomet. Chem.*, 1981, **213**, 175; E. Sappa, A. M. Manotti Lanfredi, and A. Tiripicchio, *J. Organomet. Chem.*, 1981, **221**, 93.
- 10 E. Sappa, M. Lanfranchi, A. Tiripicchio, and M. Tiripicchio Camellini, *J. Chem. Soc., Chem. Commun.*, 1981, 995.
- 11 A. J. Carty, Xth International Conference on Organometallic Chemistry, Toronto, 1981; *Pure Appl. Chem.*, in the press.