Synthesis and Crystal Structure of $(\eta\text{-}C_5H_5)_2Ni_2Ru_2(CO)_6[C_2(H)C(=CH_2)CH_3]$. A New Heterometallic Cluster with an Uncommon Metal Atom Framework

MAURIZIO LANFRANCHI, ANTONIO TIRIPICCHIO*, MARISA TIRIPICCHIO CAMELLINI

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

OLIMPIA GAMBINO and ENRICO SAPPA*

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

Received January 4, 1982

The potential utility of the homo- and heterometallic clusters as homogeneous catalysts is currently recognized [1]. However only in a very limited number of examples has the certainty been gained that the cluster itself acts as a catalyst. The use of chiral clusters has been proposed [2] because the ensuing asymmetrical syntheses would confirm the catalytic role of the clusters.

We recently reported a very simple synthetic route for a chiral cluster, $(\eta\text{-}C_5H_5)_2NiRu_2(CO)_3(\mu_3\text{-}CO)(C_2Ph_2)$ (complex I) [3]. However, the diphenylacetylene ligand is unsuitable for a study of the catalytic properties of the cluster. For this reason we attempted the synthesis of the homologue of I with a prochiral alkyne, such as isopropenyl-acetylene.

We report here the synthesis and the crystal structure of the major product of this new reaction, the complex $(\eta\text{-}C_5H_5)_2Ni_2Ru_2(CO)_6[C_2(H)C(=CH_2)CH_3]$, (complex II).

Complex II was obtained, with a procedure analogous to the one leading to I, by reacting $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ with a 1.5 molar excess of isopropenyl-acetylene in refluxing heptane, under dry nitrogen for 180 min. The resulting green-brown solution is then evaporated under vacuum and the residual dissolved in octane; to this solution $Ru_3(CO)_{12}$ is added (in 1:1 molar amount with respect of the nickel). After 20 min reflux under nitrogen, the solution is evaporated under vacuum and the residual, dissolved in $CHCl_3$, is purified on t.l.c. preparative plates. Some products (in trace amounts) are still under investigation; $(\eta\text{-}C_5H_5)NiRu_3(CO)_9[C_2(H)C(=CH_2)(CH_3)]$ (trace amounts, complex III) [4, 5], and $[(\eta\text{-}C_5H_5)Ru(CO)_2]_2$ (5% yields on ruthenium) were identified together with complex II (40% yields on ruthenium).

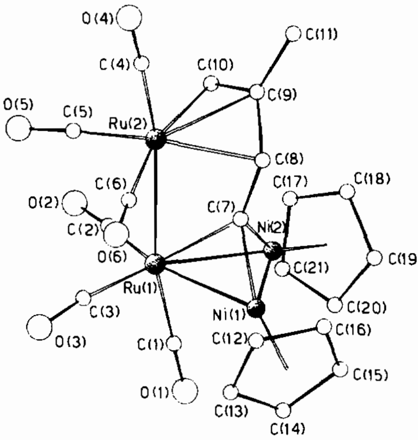

Fig. 1. The molecular structure of $(\eta\text{-}C_5H_5)_2Ni_2Ru_2(CO)_6[C_2(H)C(=CH_2)CH_3]$. Important bond lengths and angles (averaged for two independent molecules): Ru(1)–Ru(2) 2.960, Ru(1)–Ni(1) 2.515, Ru(1)–Ni(2) 2.495, Ni(1)–Ni(2) 2.368, Ru(1)–C(7) 2.06, Ru(2)–C(8) 2.17, Ru(2)–C(9) 2.25, Ru(2)–C(10) 2.26, Ni(1)–C(7) 1.83, Ni(2)–C(7) 1.85, C(7)–C(8) 1.45, C(8)–C(9) 1.44, C(9)–C(10) 1.45, C(9)–C(11) 1.52 Å; Ru(2)–Ru(1)–Ni(1) 91.4 Ru(2)–Ru(1)–Ni(2) 94.7, Ni(1)–Ru(1)–Ni(2) 56.4, Ru(1)–Ni(1)–Ni(2) 61.1, Ru(1)–Ni(2)–Ni(1) 61.9°. E.s.d.'s metal–metal 0.006–0.008, metal–C 0.02–0.03, C–C 0.04 Å, metal–metal–metal 0.1–0.2°.

The elemental analyses for II were satisfactory. The i.r. spectrum (heptane solution) in the ν_{CO} region is: 2068 vs, 2020 vs, 2008 s, 1995 s, 1960 vs, cm^{-1}.

In the ^1H n.m.r. spectrum (CCl_4, τ) the following signals were detected (integration in parentheses); 3.5 s(1), 5.04 s(5), 5.08 s(5), 7.65 s(3), 7.85 s(1), 8.60 s(1). These agree only partially with the solid state structure, as the two signals at higher field would be typical on uncoordinated $CH_{\overline{n}}$ groups.

The complex is decomposed in the introduction system of the mass spectrometer. Black, flat crystals of II were obtained by cooling heptane–chloroform solution of the complex (kept under nitrogen) for some days at −10 °C.

Crystal data: $C_{21}H_{16}O_6Ni_2Ru_2$, M = 683.91, triclinic, space group $P\bar{1}$, a = 16.728(13), b = 16.747(11), c = 8.409(8) Å, V = 2247(3) Å^3, Z = 4, D_c = 2.02 g cm^{-3}; μ(MoKα) = 29.88 cm^{-1}. The intensities of 6128 independent reflections were collected on a Siemens AED diffractometer (with θ in the range 3–23°), using Nb-filtered Mo-Kα radiation and the θ–2θ scan technique. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares on the basis of

---

*Authors to whom correspondence should be addressed.

0020-1693/82/0000-0000/$02.75

TABLE I. Fractional Atomic Co-ordinates ($\times 10^4$) with e.s.d.'s in Parentheses.

Atom	X/A	Y/B	Z/C	Atom	X/A	Y/B	Z/C
Ru1A	600(2)	1845(2)	3636(3)	C18A	2397(14)	4108(15)	6165(33)
Ru2A	1770(2)	1719(2)	1055(3)	C19A	1745(14)	4524(15)	6395(33)
Ru1B	3991(2)	−2602(2)	408(3)	C20A	1159(14)	4085(15)	7309(33)
Ru2B	3635(2)	−1047(2)	2267(4)	C21A	1449(14)	3396(15)	7643(33)
Ni1A	334(2)	3143(3)	2903(5)	O1B	4391(19)	−4240(21)	−845(39)
Ni2A	1326(3)	3273(3)	5061(5)	O2B	2868(17)	−2700(16)	−2521(34)
Ni1B	4396(2)	−3037(3)	2970(5)	O3B	5486(18)	−1523(18)	−750(34)
Ni2B	3025(2)	−3540(2)	1880(5)	O4B	3443(19)	663(21)	3761(40)
O1A	−486(15)	2348(15)	6242(31)	O5B	3622(19)	−662(19)	−1111(40)
O2A	1266(18)	766(19)	5576(37)	O6B	5458(20)	−495(18)	3295(36)
O3A	−760(20)	499(20)	1742(39)	C1B	4224(23)	−3570(26)	−316(47)
O4A	2777(18)	1260(18)	−1751(38)	C2B	3289(23)	−2654(23)	−1330(47)
O5A	1523(16)	0(18)	1814(33)	C3B	4939(23)	−1940(23)	−263(45)
O6A	244(17)	1353(16)	−1252(33)	C4B	3498(24)	−9(27)	3166(49)
C1A	−84(23)	2156(23)	5250(49)	C5B	3668(23)	−837(24)	223(50)
C2A	1027(24)	1208(25)	4784(51)	C6B	4812(32)	−666(30)	2858(58)
C3A	−184(26)	1002(26)	2480(50)	C7B	3604(17)	−2467(18)	2728(35)
C4A	2417(26)	1464(26)	−613(54)	C8B	3333(19)	−1881(19)	3993(38)
C5A	1640(25)	682(28)	1511(51)	C9B	2613(20)	−1552(21)	3743(42)
C6A	796(20)	1466(20)	−360(40)	C10B	2307(22)	−1698(22)	2052(44)
C7A	1325(19)	2846(19)	2838(37)	C11B	2317(24)	−1023(25)	5227(50)
C8A	1964(20)	3055(20)	1754(40)	C12B	5182(19)	−2562(14)	5102(33)
C9A	2766(20)	2905(20)	1918(39)	C13B	4679(19)	−3349(14)	5234(33)
C10A	2836(20)	2323(21)	2958(41)	C14B	4834(19)	−3963(14)	3935(33)
C11A	3477(23)	3284(23)	1052(46)	C15B	5433(19)	−3555(14)	3000(33)
C12A	−298(18)	3191(17)	739(27)	C16B	5648(19)	−2689(14)	3722(33)
C13A	−856(18)	2937(17)	1895(27)	C17B	1880(16)	−4231(17)	605(27)
C14A	−724(18)	3594(17)	3288(27)	C18B	2410(16)	−4776(17)	691(27)
C15A	−84(18)	4255(17)	2993(27)	C19B	2606(16)	−4746(17)	2355(27)
C16A	180(18)	4006(17)	1418(27)	C20B	2196(16)	−4182(17)	3298(27)
C17A	2215(14)	3410(15)	6936(33)	C21B	1747(16)	−3864(17)	2216(27)

1640 observed reflections [having $I \geqslant 2\sigma(I)$] to a R value of 4.6%. The fractional atomic coordinates are given ~~in~~ Table I.

The structure of II is represented in Fig. 1, together with the more significant bond distances and angles. The metal atom framework consists of an isosceles triangle of two nickel and one ruthenium atoms, Ni(1), Ni(2), Ru(1), with another ruthenium atom, Ru(2), apically bound to Ru(1). This metal-atom arrangement is unprecedented for neutral, hetero-metallic clusters: the only other example to our knowledge is the homometallic $[H_4Re_4(CO)_{15}]^{2-}$ anion [6].

In the $Ni_2Ru(1)$ triangle both the Ru–Ni and the Ni–Ni bonds are rather short in comparison with those reported for the mixed ruthenium–nickel clusters [7] and for the $(\eta\text{-}C_5H_5)_2Ni_2$ (alkyne) complexes [8]. On the contrary the Ru–Ru bond is longer than those generally found in closed or open ruthenium frameworks [9].

The two cyclopentadienyl ligands are η-coordinated to the Ni atoms and the six carbonyl groups are terminally bound, three to each Ru atom. The isopropenylacetylene ligand interacts with all the metal atoms through a complex bonding system involving both the former triple and the double bond, so that an extensive delocalized bonding is observed in the four-carbon coordinated chain (as shown by the C–C bond distances ranging from 1.43 to 1.46 Å). The bonding situation of the terminal C(7) atom capping the $Ni_2Ru(1)$ triangle is noteworthy. The interaction with the metal cluster of the double bond of the isopropenyl group has been already observed only in the homometallic ruthenium complex $Ru_3(CO)_8(C_{10}H_{12})$ [10].

The electronic counting for the metal atoms agrees with the E.A.N. rule when considering the isopropenylacetylene ligand as a six electron donor towards the metals.

Anomalous behaviour of the isopropenylacetylene with respect of the other alkynes in their coordination to ruthenium [8] or ruthenium–nickel clusters [11] has already been observed; however, the striking difference in the main reaction products when diphenylacetylene (complex I) and isopropenylacetylene (complex II) are reacted under the same conditions is noteworthy.

The formation mechanisms of I and II are at present under investigation, as is the identification of the minor products of the reactions.

References

1 B. F. G. Johnson, Ed., 'Transition Metal Clusters', Wiley, Interscience (1980).

2 F. Richter and H. Vahrenkamp, *Angew. Chem. Int. Ed., 18,* 531 (1979).
R. Whyman, in B. F. G. Johnson, Ed., 'Transition Metal Clusters', Wiley, Interscience, 569 (1980).

3 E. Sappa, A. Tiripicchio and M. Tiripicchio Camellini, *J. Organometal. Chem., 213,* 175 (1981).

4 A. J. Carty, M. Castiglioni, E. Sappa and A. Tiripicchio, Communication to the EUCHEM Congress, Sept. 28–30, Venice, Italy.

5 E. Sappa, A. Tiripiccho and M. Tiripicchio Camellini, *J. Chem. Soc. Chem. Comm.,* 254 (1979).

6 V. G. Albano, G. Ciani, M. Freni and P. Romiti, *J. Organometal. Chem., 96,* 259 (1975).

7 E. Sappa, A. M. Manotti Lanfredi and A. Tiripicchio, *J. Organometal. Chem.,* in the press and references therein.

8 Y. Wang and P. Coppens, *Inorg. Chem., 15,* 1122 (1976).
O. S. Mills and B. W. Shaw, *J. Organometal. Chem., 11,* 595 (1968).
E. L. Muetterties, W. R. Pretzer, M. G. Thomas, B. F. Beier, D. L. Thorn, V. W. Day and B. A. Anderson, *J. Am. Chem. Soc., 100,* 2090 (1978).

9 E. Rosenberg, S. Aime, L. Milone, E. Sappa, A. Tiripicchio and A. M. Manotti Lanfredi, *J. Chem. Soc. Dalton,* in the press and references therein.
E. Sappa, A. M. Manotti Lanfredi and A. Tiripicchio, *Inorg. Chim. Acta, 36,* 197 (1979).

10 O. Gambino, E. Sappa, A. M. Manotti Lanfredi and A. Tiripicchio, *Inorg. Chim. Acta, 36,* 189 (1979).

11 A. J. Carty, E. Sappa, A. Tiripicchio and M. Tiripicchio Camellini, XIV Congr. Naz. Chim. Inorg., Sept. 14–17, Turin, Italy (C-6).