Rhodium Clusters Substituted by Cycloheptatrienyl Ligands: Synthesis and Solid-State Structure of $[Rh_{11}(CO)_{14}(\mu_3\text{-}\eta^2\text{:}\eta^3\text{:}\eta^2\text{-}C_7H_7)_3]$

Roberto Della Pergola,*[a] Emanuela Comensoli,[b] Luigi Garlaschelli,[b] Mario Manassero,*[c] Mirella Sansoni,[c] and Donatella Strumolo[b]

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The cluster $[Rh_{11}(CO)_{14}(C_7H_7)_3]$ (**1**) was obtained from the reaction of $[Rh_6(CO)_{16}]$ and an excess of cycloheptatriene in refluxing toluene. Initially, the substituted cluster $[Rh_6(CO)_{13}(C_7H_8)]$ (**2**) could be identified spectroscopically, which is transformed into **1** after prolonged refluxing. In the solid state, the eleven rhodium atoms define a trioctahedral metal cage, condensed through a common edge. The three planar, equivalent C_7 rings sit on the top of triangular faces. The spectroscopic characterisation of the product is hampered by its low solubility.

Ligands derived from cycloheptatriene are widely employed in organometallic chemistry; mononuclear[1] and cluster compounds[2] containing such a ring are well documented in the literature. When supported by a cluster, the C_7 rings can bind one, two or three metal atoms. Relevant examples of these different bonding modes are: (i) $[Ru_6C(CO)_{11}(C_7H_9)(C_7H_7)]$[3] and $[Co_4(CO)_6(C_7H_9)(C_7H_7)]$,[4] where η^5-C_7H_9 and μ_3-η^7-C_7H_7 binding modes are displayed in the same molecule, (ii) $[Ru_4(CO)_7(C_7H_7)_2]$, which contains edge-bridging μ_2-η^3:η^4 units,[5] and (iii) $[Ru_6C(CO)_{14}(C_7H_8)]$, where a facial μ_3-η^2:η^2:η^2 binding mode is present.[3] Upon coordination to several metal atoms, the reactivity of the ring is modified, and the hapticity of the ligand can be changed either by a ring contraction,[3] by reductive coupling,[6] or by a ligand-to-ligand hydrogen transfer.[3,4]

We have recently isolated $[Ir_6(CO)_{13}(C_7H_8)]$, and described its peculiar reactivity toward reducing agents, which is assisted by a reversible modification of the bonding mode of the cyclic ligand.[7]

The substitution of rhodium clusters with carbocyclic ligands is relatively unexplored: reactions of $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ with polyenes have been described,[8] but only $[Rh_6(CO)_{14}(\eta^4\text{-}C_6H_8)]$,[9] $[Rh_4(CO)_8(\mu_3\text{-}C_8H_8)]$ and $[Rh_4(CO)_6(\mu_3\text{-}C_8H_6R_2)(\eta^4\text{-}C_8H_6R_2)]$[10] have been structurally characterised. For these reasons we have re-examined the substitution of $[Rh_6(CO)_{16}]$ with cycloheptatriene. We found a behaviour different from that already reported,[8] and from that of $Ir_6(CO)_{16}$,[7] which allowed us to isolate a new rhodium cluster that is highly substituted by the C_7 ring.

Results

The carbonyl substitution of $Rh_6(CO)_{16}$ with cycloheptatriene proceeds in boiling toluene. After about six hours most of the starting material has been converted into a new, soluble cluster. The infrared spectrum of the toluene solution allows the unequivocal identification of this primary product as $[Rh_6(CO)_{13}(C_7H_8)]$ (**2**), since its carbonyl stretching bands (2093s, 2064vs, 2035s, 2006m, 1794m cm^{-1}) are almost superimposable with those of the corresponding iridium analogue $[Ir_6(CO)_{13}(C_7H_8)]$.[7] All attempts to grow crystals, isolate in the solid state, purify, or convert **2** into an anionic derivative failed, owing to its high solubility and moderate stability. Currently, we are trying to identify the decomposition products, to reconstruct the steps of the subsequent cluster build-up. At this early stage of the reaction, a brown microcrystalline precipitate is also present, which can be easily confused with unreacted $Rh_6(CO)_{16}$.[8] However, $[Ir_6(CO)_{13}(C_7H_8)]$ is poorly soluble in toluene and it crystallizes directly on cooling the reaction mixture.[7] Therefore we measured the crystallographic parameters of the dark solid residue, and found a com-

[a] Dipartimento di Scienze dell' Ambiente e del Territorio – Università di Milano Bicocca
Piazza della Scienza 1, 20126 Milano, Italy
Fax: (internat.) +39-026448-2890
E-mail: roberto.dellapergola@unimib.it
[b] Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Milano
Via G. Venezian 21, 20133 Milano, Italy
[c] Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano
Via G. Venezian 21, 20133 Milano, Italy
E-mail: m.manassero@istm.cnr.it
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pletely unexpected unit cell. Thus, the course of the reaction was investigated more deeply. The solution was subjected to a few additional cycles of heating and cooling: after 10 additional hours the solution was colourless, and **2** had been completely converted into a material that is very insoluble in THF, CH_2Cl_2, MeCN and hydrocarbon solvents. Several of the well-shaped crystals were big enough for a X-ray analysis, and a structural characterisation of the new cluster $[Rh_{11}(CO)_{14}(C_7H_7)_3]$ (**1**) was performed. The powder residue could only be partially characterised. The elemental analysis established a Rh/C_7 ring ratio of 2, and its infrared spectrum, as a nujol mull, showed bands at 1977m, 1954s, 1804m cm^{-1}. It was found, by XRPD, to be poorly crystalline. These data suggest that this material, which is the main product of the reaction, is composed of highly substituted clusters whose formulation can be related neither to **1** nor to **2**.

The solid state structure of **1**, together with the numbering scheme, is shown in Figure 1. Figure 2 shows, with two different orientations, the connectivity of the CO's and the C_7H_7 rings to the metallic framework, which can be described as three octahedra, mutually fused through a face and all sharing a common edge [Rh(1)−Rh(1′)]. Owing to the crystallographic symmetry, only three metal atoms, three independent carbonyl groups and four carbon atoms of the C_7H_7 ring occupy the asymmetric unit. The molecule contains terminal [CO(1)], edge-bridging [CO(2)] and face-bridging [CO(3)] CO ligands, 15 sites in total, which are all indicated in the figures. However, we strongly believe that **1** contains only 14 CO molecules, and that the six equivalent

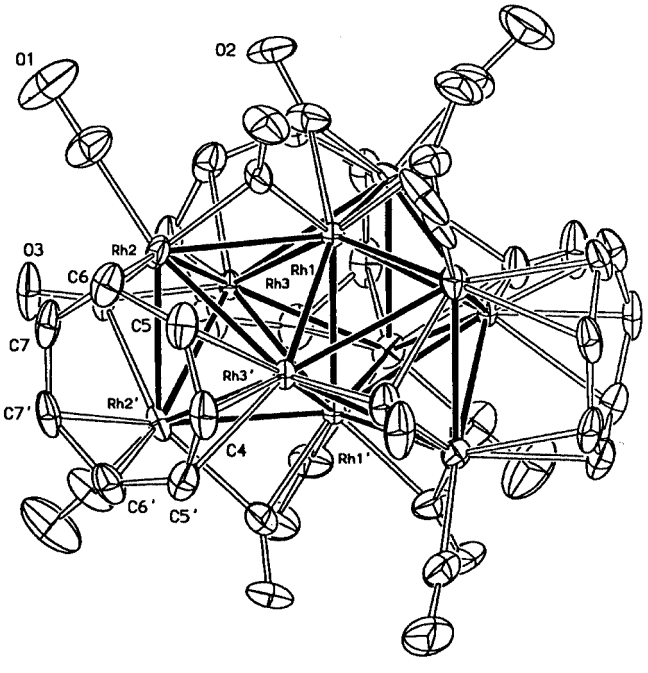

Figure 1. The solid state structure of $[Rh_{11}(CO)_{14}(C_7H_7)_3]$; relevant bond lengths (Å): Rh(1)−Rh(1′) 2.821(1), Rh(1)−Rh(2) 2.684(1), Rh(1)−Rh(3) 2.720(1), Rh(2)−Rh(2′) 2.733(1), Rh(2)−Rh(3) 2.885(1), Rh(2)−Rh(3′) 2.855(1), Rh(3)−C(4) 2.142(4), Rh(3)−C(5) 2.323(4), Rh(2)−C(6) 2.159(4), Rh(2)−C(7) 2.209(5); average C−C(ring) 1.416

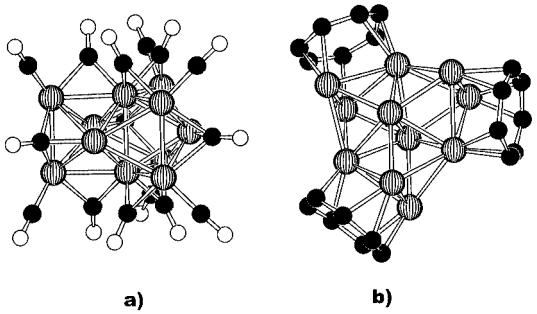

Figure 2. The disposition of the carbonyls (a) and the C_7H_7 (b) around the metallic framework of $[Rh_{11}(CO)_{14}(C_7H_7)_3]$

CO(2) sites are randomly occupied by five ligands. As a matter of fact the occupancy factor of CO(2) is lower than unity, and close to the expected value of 5/6 (0.83). Under this assumption, **1** possesses 148 valence electrons, a number which has been observed in Rh,[11] Pt−Rh[12] or Ir[13] clusters with the same framework. The three independent metal atoms are very different for the number of Rh−Rh, Rh−CO and $Rh-C_{ring}$ connectivities; however, local electron counts[13] at the three sites differ by less than one electron, and the small discrepancies cannot be rationalized in terms of bond-length variations, even if the asymmetry of the face bridging CO(3) [2.335(3) Å for Rh(2)−CO(3) and 1.977(7) for Rh(3)−CO(3)] is consistent with the unbalanced distribution of electrons. For example, Rh(1) has a (formal) excess of one electron, but the longest bonds within the cluster are the Rh(2)−Rh(3) interactions. It is likely that the lengths of the Rh−Rh bonds reflect the steric and electronic requirements of the carbocycle. In keeping with this, the bond lengths of the organic unit are spread over a wide range: 2.142(4)−2.323(4) for $Rh-C_{ring}$ and 1.378(6)−1.447(7) Å for C−C bonds.

The almost planar cycloheptatrienyl rings are bound to triangular faces in the μ_3-η^2:η^3:η^2 fashion and are coordinated through one allylic system to Rh(3) and through two C=C double bonds to Rh(2). A slightly different arrangement for the same ligand has frequently been observed: in the μ_3-η^2:η^3:η^3 bonding mode one carbon atom, shared by two allylic moieties, is connected to two metal atoms with comparable distances.[4,7] In **1** the two external atoms of the allylic systems are very far from the nonbonded rhodium atom [Rh(2)−C(5) is about 2.9 Å] and the cluster can be classified as a genuine example of μ_3-η^2:η^3:η^2 hapticity. In any case, the neutral ligand must be considered as a seven-electron donor. Alternatively, the molecule can be described as being derived from the homoleptic $[Rh_{11}(CO)_{23}]^{3-}$,[11] by formal substitution of nine CO's with three tropylium cations ($[C_7H_7]^+$ is a six-electron donor).

Unfortunately, the analytical and spectroscopic characterisation of **1** is hampered by its low solubility, which is not unexpected for a neutral, high-nuclearity cluster. Even if the compound were available in larger amounts, it is unlikely that the number of CO ligands could be confirmed by microanalysis, since the differences would be below the experimental errors. To confirm the presence of **1** among

the products of the reaction, the determination of the cell parameters is more straightforward than infrared spectroscopy as five crystals, selected from among the bigger ones with difficulty, were not sufficient to record an infrared spectrum of reasonable quality.

Despite the lack of spectroscopic data on $[Rh_{11}(CO)_{14}(C_7H_7)_3]$, this compound is important since it sheds a new light on the reactivity of rhodium clusters[8,10] with cyclic unsaturated hydrocarbons: the carbonyl substitution can be accompanied by unpredictable cluster reconstruction, leading to highly substituted, high-nuclearity clusters. The reproducible preparation and the symmetrical structure of **1** are strong evidences of its high stability. Among the group 9 metal clusters it may be compared to $[Ir_7(CO)_{12}(C_8H_{12})(C_8H_{11})(C_8H_{10})]$, which shows stages of cyclooctadiene dehydrogenation.[14]

Experimental Section

In a typical preparation, $[Rh_6(CO_{16}]$ (0.30 g, 0.28 mmol) and cycloheptatriene (0.3 mL, 3 mmol) were suspended in 10 mL of toluene. The mixture was refluxed for five days, without stirring, switching the heating on and off at the beginning and at the end of the day's work. The residue, insoluble in most common solvents, was collected by filtration, and washed with toluene. $[Rh_2(CO)_4(C_7H_7)]_n$: calcd. for C 32.3, H 1.7; found C 31.7, H 1.9.

Well-shaped, prismatic crystals of **1** were selected under the lens of a microscope and used for characterisation.

Crystal data and other experimental details are summarized in Table 1. The diffraction experiment was carried out on a Bruker SMART CCD area-detector diffractometer at 223 K using Mo-K_α radiation (λ = 0.71073 Å) with a graphite monochromator in the incident beam. Intensity data were processed with the software SAINT,[15a] and an empirical absorption correction was applied (SADABS).[15b] The calculations were performed using the Personal Structure Determination Package[16] and the physical constants tabulated therein. Scattering factors and anomalous dispersion corrections were taken from ref.[17] The structure was solved by direct methods (SHELXS 86)[18] and refined by full-matrix least-squares using all reflections and minimizing the function $\Sigma w(F_o^2 - kF_c^2)^2$ (refinement on F^2). Anisotropic thermal factors were refined for all the non-hydrogen atoms. Hydrogen atoms were placed in their ideal positions and not refined. In the final difference Fourier map the maximum residual electron density was 1.40(49) e·Å^{-3} at 0.66 Å from Rh(2).

Table 1. Selected crystallographic data (more detailed information can be found in the Supporting Information)

Formula	$C_{35}H_{21}O_{14}Rh_{11}$
M	1797.50
Crystal system	hexagonal
Space group	$P6_3/m$
a (Å)	11.821(1)
c (Å)	16.492(2)
U (Å^3)	1995.8(4)
Z	2
T (K)	223
θ-range/°	3−26
Reciprocal space explored	hemisphere
No. of reflections (total; independent)	16288, 2095
R_{int}	0.059
Final R_2 and R_{2w} indices (F^2, all reflections)	0.047, 0.054
Conventional R_1 index [$I > 2\sigma(I)$]	0.028
Reflections with $I > 2\sigma(I)$	1440

CCDC-194777 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or at Cambridge crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-122/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] M. L. H. Green, D. K. P. Ng, *Chem. Rev.* **1995**, *95*, 439−473.
[2] H. Wadepohl, *Coord. Chem. Rev.* **1999**, *185−186*, 551−568.
[3] D. Braga, F. Grepioni, L. Scaccianoce, B. F. G. Johnson, *J. Chem. Soc., Dalton Trans.* **1998**, 1321−1325.
[4] H. Wadepohl, S. Gebert, H. Pritzkow, F. Grepioni, D. Braga, *Chem. Eur. J.* **1998**, *4*, 279−288.
[5] D. Braga, P. J. Dyson, F. Grepioni, B. F. G. Johnson, C. M. Martin, L. Scaccianoce, A. Steiner, *Chem. Commun.* **1997**, 1259−1260.
[6] H. Wadepohl, S. Gebert, H. Pritzkow, D. Osella, C. Nervi, J. Fiedler, *Eur. J. Inorg. Chem.* **2000**, 1833−1843.
[7] R. Della Pergola, A. Bianchi, F. Fabrizi de Biani, L. Garlaschelli, M. Manassero, M. Sansoni, D. Strumolo, P. Zanello, *Organometallics* **2002**, in press
[8] T. Kitamura, T. Joh, *J. Organomet. Chem.* **1974**, *65*, 235−243.
[9] P. J. Dyson, S. L. Ingham, B. F. G. Johnson, A. J. Blake, *J. Organomet. Chem.* **1995**, *498*, 237−240.
[10] H. Wadepohl, R. Merkel, H. Pritzkow, S. Rihm, *J. Chem. Soc., Dalton Trans.* **2001**, 3617−3625.
[11] A. Fumagalli, S. Martinengo, G. Ciani, A. Sironi, B. T. Heaton, *J. Chem. Soc., Dalton Trans.* **1988**, 163−171.
[12] A. Fumagalli, S. Martinengo, G. Ciani, *J. Organomet. Chem.* **1984**, *273*, C46−C49.
[13] R. Della Pergola, L. Garlaschelli, M. Manassero, M. Sansoni, *J. Cluster Sci.* **1999**, *10*, 109−119 and references therein
[14] C. G. Pierpont, *Inorg. Chem.* **1979**, *18*, 2972−2977.
[15] [15a] SAINT Reference manual, Siemens Energy and Automation, Madison, WI, **1994−1996**. [15b] G. M. Sheldrick, SADABS, Empirical Absorption Correction Program, University of Gottingen, **1997**.
[16] [16a] B. A. Frenz, *Comput. Phys.* **1988**, *2*, 42. [16b] Crystallographic Computing 5, Oxford University Press: Oxford, U. K., **1991**; Chapter 11, p. 126.
[17] International Tables for X-ray Crystallography, Vol.4, Kynoch Press, Birmingham, **1974**.
[18] G. M. Sheldrick, SHELXS-86, Program for the solution of crystal structures, University of Gottingen, Germany, **1985**.

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