Inorganic Chemistry
Communication
pubs.acs.org/IC

New High-Nuclearity Carbonyl and Carbonyl-Substituted Rhodium Clusters and Their Relationships with Polyicosahedral Carbonyl-Substituted Palladium- and Gold-Thiolates

Dmitriy S. Dolzhnikov,[†] Maria C. Iapalucci, Giuliano Longoni, Cristina Tiozzo,[‡] Stefano Zacchini, and Cristina Femoni*

Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

Ⓢ *Supporting Information*

ABSTRACT: A reinvestigation of the synthesis of $[H_{5-n}Rh_{13}(CO)_{24}]^{n-}$ (n = 2, 3) led to isolation of a series of Rh_{19}, Rh_{26}, and Rh_{33} high-nuclearity carbonyl and carbonyl-substituted rhodium clusters. The $[Rh_{19}(CO)_{31}]^{5-}$ (**1**) is electronically equivalent with $[Pt_{19}(CO)_{22}]^{4-}$, but poor crystal diffraction data of all salts obtained to date have prevented its geometrical analysis. The structures of $Rh_{26}(CO)_{29}(CH_3CN)_{11}$ (**2**) as **2**·$2CH_3CN$ and $[Rh_{33}(CO)_{47}]^{5-}$ (**3**) as $[NEt_4]_5$[**3**]·Me_2CO were determined from complete X-ray diffraction determinations. The latter two species adopt polyicosahedral metal frameworks, and notably, $[Rh_{33}(CO)_{47}]^{5-}$ represents the molecular group 9 metal carbonyl cluster of highest nuclearity so far reported.

An impressive series of nanosized molecular metal clusters, anionic (e.g., $[Pt_{38}(CO)_{44}]^{2-}$,[1,2] $[Ni_{32}Pt_{24}(CO)_{56}]^{6-}$,[3] $[Au_{34}Fe_{14}(CO)_{50}]^{8-}$[4]), neutral (e.g., $Pd_{69}(CO)_{36}(PEt_3)_{18}$,[5,6] $Pd_{145}(CO)_{\sim 70}(PEt_3)_{30}$,[6,7] $Pd_{165-x}Pt_x(CO)_{72}(PPh_3)_{20}$ ($x \sim 8$),[6,8] $Au_{18}Ag_{20}(p\text{-}Tol_3P)_{12}Cl_{14}$,[9] $Au_{38}(S{-}CH_2{-}CH_2{-}Ph)_{24}$,[10] $Au_{102}(S{-}p{-}C_6H_4{-}COOH)_{44}$),[11] and cationic (e.g., $[Au_6Ag_{13}(dppm)_3(-C\equiv C-R)_{14}]^{5+}$),[12] has been synthesized and structurally characterized. As shown by the few leading examples, these clusters only comprise metals of groups 10 and 11. Whereas the so far known homometallic Pt and bimetallic Ni−Pd and Ni−Pt clusters may be systematically derived from chunks of close-packed metal lattices,[13] both homo- and bimetallic clusters of the coinage metals, as well as the homometallic Pd clusters, display a distinct propensity for condensed, fused, or interpenetrating centered icosahedral frameworks.[6] Species of comparable metal nuclearities and structures involving group 9 metal atoms are unknown. Prior to this report, the previous largest nuclearity was held by the homometallic $[H_{4/3}Rh_{22}(CO)_{35}]^{4-/5-}$[14,15] and $[Rh_{22}(CO)_{37}]^{4-}$[16] and by the nitride $[H_xRh_{28}N_4(CO)_{41}]^{4-}$ clusters, which are based on chunks of *bcc* and *cp* metal lattices.[17] We here report the isolation and characterization of new Rh clusters which push a little farther the maximum metal nuclearity but, most interestingly, extend the interpenetrating icosahedral growth of Pd and Au also to Rh.

These new species all originate from a reinvestigation of the reactions of $Rh_4(CO)_{12}$ with NaOH in miscellaneous solvents. The original reaction[18] of $Rh_4(CO)_{12}$ induced by NaOH (Rh/OH^- = 6.5) in boiling isopropyl alcohol under a H_2 atmosphere affords $[H_3Rh_{13}(CO)_{24}]^{2-}$ in good yields (ca. 85% based on Rh). The remaining 15% of Rh was later identified to be $[H_3Rh_{22}(CO)_{35}]^{5-}$, which has been reported elsewhere in full detail.[15] ESI−MS monitoring of the crude CH_3CN extract of $[H_3Rh_{22}(CO)_{35}]^{5-}$ also disclosed the presence of very minor signals which could be attributed to an unknown $[Rh_{26}(CO)_{40-m}]^{2-}$ species. This prompted a further investigation of the reaction under slightly different experimental conditions, which led to the isolation of $[Rh_{19}(CO)_{31}]^{5-}$ (**1**), $Rh_{26}(CO)_{29}(CH_3CN)_{11}$ (**2**), and $[Rh_{33}(CO)_{47}]^{5-}$ (**3**). Of these, **2** and **3** represent the highest nuclearity Rh carbonyl clusters not containing interstitial heteroatoms so far reported.

The brown **1** cluster was obtained in good yields (∼ 40%) by the refluxing of a solution of $Rh_4(CO)_{12}$ and NaOH (Rh/OH^- = 3.2) in isopropyl alcohol, for 1 h in a microwave reactor, under a N_2 rather than a H_2 atmosphere. This compound has been isolated and characterized by elemental analysis, IR, and ESI-MS as the $[NEt_4]_5[Rh_{19}(CO)_{31}]$ salt (νCO in CH_3CN at 1973(*s*), 1818(*m*) cm^{-1}). In particular, its ESI-MS shows sets of peaks due to $\{[NEt_4]_3[Rh_{19}(CO)_{31}]\}^{2-}$ (m/z 1607), $\{[NEt_4]_2[Rh_{19}CO)_{31}]\}^{2-}$ (m/z 1542), $\{[NEt_4][Rh_{19}(CO)_{31}]\}^{2-}$ (m/z 1476), and $[Rh_{19}(CO)_{31}]^{3-}$ (m/z 940), accompanied by those arising from the progressive loss of four COs. Unfortunately, all crystals of $[Rh_{19}(CO)_{31}]^{5-}$ were very poorly diffracting and did not provide an X-ray structural determination. The brown neutral carbonyl-substituted **2** species (ν_{CO} in CH_3CN at 2010(*s,sh*), 1997(vs), 1849(*ms,br*), and 1811(*sh*) cm^{-1}) was obtained in modest yields (ca. 10%) by controlled addition of H_2SO_4 to CH_3CN solutions of $[H_3Rh_{22}(CO)_{35}]^{5-}$. As suggested by ESI-MS monitoring of the reaction solution, which shows a peak at 1898 m/z due to $\{[Rh_{26}(CO)_{40}]\}^{2-}$, accompanied by those arising from a progressive loss of CO's, the low yields are likely justified by the formation of a mixture of $Rh_{26}(CO)_{40-x}(CH_3CN)_x$ (x = 0−11) species. The brown **3** penta-anion (νCO in CH_3CN at 2012(vs), 1993(*sh*), 1976(*sh*), 1835(*ms*), and 1813(*ms*) cm^{-1}) was obtained in fair yields (∼ 25%) by the thermal reduction of $Rh_4(CO)_{12}$ with NaOH (Rh/OH^- = 6.5) in isopropyl alcohol, under a H_2 atmosphere for up to 72 h. In CH_3CN solutions, **1**, **2**, and **3** do not display ^1H NMR signals indicative of the presence of hydride atoms.

Received: May 31, 2012
Published: October 8, 2012

dx.doi.org/10.1021/ic3011508 | *Inorg. Chem.* 2012, 51, 11214−11216

Solvated crystals of **2**·2CH_3CN[19] and **3**$[NEt_4]_5$·3$(CH_3)_2CO$[20] have been characterized by X-ray diffraction. The metal framework of **2**, shown in Figure 1,[21] may be derived from the interpenetration of four centered icosahedral Rh_{13} moieties and therefore presents four interstitial Rh atoms (blackened spheres in Figure 1). Interestingly, it conforms to the growth pattern based on interpenetration of six double icosahedra (DI) proposed by Farges[22] and extended by Mednikov and Dahl to Ni–Pd and Pd carbonyl-substituted clusters.[6,23] An identical Pd_{26} metal frame constitutes the inner metal core of the previously reported bimetallic $Pd_{29}Ni_3(CO)_{22}(PMe_3)_{13}$ species.[6,24]

Figure 1. View of the metal frame of **2** pointing out the interstitial Rh_4 tetrahedron. Each Rh–Rh edge of the inner tetrahedron is interstitially lodged in a Rh_{19} DI.

As shown in Figure 2,[21] the ligand shell of the Rh_{26} cluster consists of 11 CH_3CN molecules and 29 carbonyl groups, 20 of which are terminally bonded.

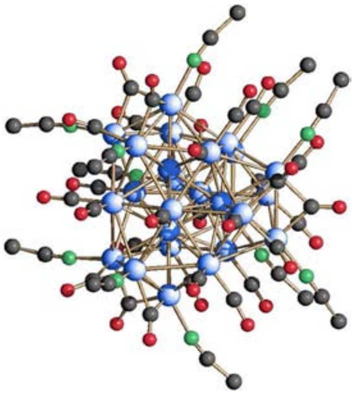


Figure 2. The molecular structure of **2** (color scheme: Rh, blue; C, gray; O, red; N, green). Hydrogen atoms have been omitted for clarity.

To our knowledge, compound **2** represents the highest nuclearity carbonyl-substituted Rh cluster so far reported (diameter of about 0.8 nm, as measured in correspondence of the nuclei of outer Rh atoms). The presence of labile CH_3CN ligands might be a prelude to possible tailoring of the cluster for use in biological domains, e.g., imaging and tagging protocols, as well as cancer cell apoptosis with low-valent clusters.[25]

The molecular structure of **3** is shown in Figure 3.[21]

Its metal frame has a discotic shape (ca. 1 × 1 × 0.5 nm, as measured in correspondence of the nuclei of outer Rh atoms) and is elucidated by the formal step-by-step construction reported in Figure 4.[21]

Similarly to **2**, the inner Rh_{19} moiety of **3** (Figure 4a) conforms to the polyicosahedral growth sequence based on interpenetrated centered icosahedra.[6] However, a small but yet significant variance occurs. The central core grows along both directions of the C_5 axis by interpenetration of two centered *arachno* Rh_{11} moieties, to give the Rh_{27} rod shown in Figure 4b. The remaining six Rh atoms, three on each side, generate four additional interpenetrated centered *arachno* Rh_{11} moieties in the back and two interpenetrated and highly distorted compact fragments in the front (Figure 4c). Altogether, there are two fully interstitial and six plus two semi-interstitial Rh atoms displaying coordination of 12 (blackened spheres), 10 (crossed spheres), and 9 (lined spheres), respectively. The latter eight semi-interstitial Rh atoms complete their coordination by binding a terminal carbonyl ligand. Each of the 23 surface Rh atoms (open spheres) also binds a terminal CO group. The remaining 16 COs are almost symmetrical edge bridges.

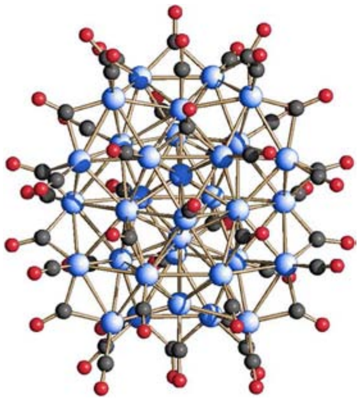
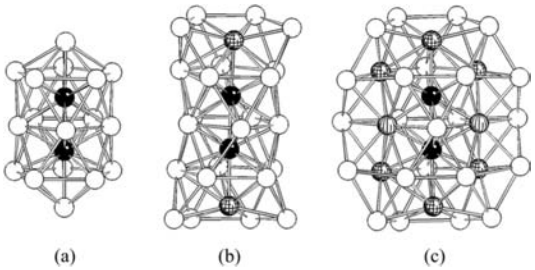


Figure 3. The molecular structure of **3** (color scheme: Rh, blue; C, gray; O, red).



(a) (b) (c)

Figure 4. Step-by-step construction of the metal frame of **3**.

The yet structurally uncharacterized cluster **1** features 238 cluster valence electrons (CVEs), like the capped pentagonal prismatic $[Pt_{19}(CO)_{22}]^{4-}$,[26a] and displays six additional CVEs with respect to the $[Pt_{19}(CO)_{17}]^{8-}$ core of $[Pt_{19}(CO)_{17}\{Cd_5(\mu\text{-}Br)_5Br_3(Me_2CO)_2\}\{Cd_5(\mu\text{-}Br)_5Br(Me_2CO)_4\}]^{2-}$.[26b] On the basis of the observed electronic differences between Rh and Pt carbonyl clusters (isoskeletal Rh clusters require more CVEs than Pt clusters),[27] it may be speculated that **1** could conform to the D_{5h} interpenetrated icosahedral model (1DI) and therefore to possess the structure shown in Figure 4a. Such a structure would not be unprecedented.[29] If so, **1** would represent a possible building block for **2** and **3**. Further studies are however necessary in order to substantiate the above speculative suggestion and chemically relate the three species.

The present work demonstrates that the polyicosahedral growth is not restricted to Pd or coinage metals and competes with *bcc* and *cp* lattices also for a metal such as Rh, even if the Rh–Rh bond energy in bulk is approximately twice as much. A few considerations may justify why this occurs. The number of CVEs can be calculated and inserted in the formula CVE = $12N + x$ introduced by Mingos[27] (N = nuclearity of the cluster). The obtained x value varies for different geometries, and it is higher in more compact metal frameworks. Clusters **2** and **3** display values of *x* of 2 and 0, respectively, versus a value of 6 for the Pd and Ni–Pd clusters whose metal kernels conform to the same DI interpenetrated growth sequence (namely, $Pd_{37}(CO)_{28}\{P(p\text{-}C_6H_4Me)_3\}_{12}$,[23] $Pd_{29}Ni_3(CO)_{22}(PMe_3)_{13}$,[24] and $Pd_{35}(CO)_{23}(PMe_3)_{15}$[24]). This difference is probably due to the presence of some wingtip atoms in the latter clusters. In any case, these *x* values are significantly lower than those of *cp* metal clusters of comparable nuclearity (e.g., $[Pt_{26}(CO)_{32}]^{2-}$,[2,30] $x = 14$; $[Ni_{13}Pd_{13}(CO)_{34}]^{4-}$,[31] $x = 20$; $[Pd_{29}(CO)_{28}(PPh_3)_7]^{2-}$,[32] $x = 14$; $[Pd_{30}(CO)_{26}(PEt_3)_{10}]$,[33] $x = 12$; $[Ni_{16}Pd_{16}(CO)_{40}]^{4-}$,[34] $x = 20$). Rh has fewer valence electrons than the group 10 and 11 metals; therefore, its clusters should acquire a greater number of CVEs from the ligands. However, the title compounds cannot gather sufficient electrons from the ligands, their number being limited by the experimental conditions; therefore, the Rh atoms maximize their average number of near neighbors (ANNs) and, consequently, their cohesive energy, by adopting interpenetrated polyicosahedral structures. For instance, the Rh kernel of **2** (6 DI) has an ANN of 7.85, whereas the isonuclear $[Pt_{26}(CO)_{32}]^{2-}$ (*hcp*) and $[Ni_{13}Pd_{13}(CO)_{34}]^{4-}$ (*ccp*) clusters display ANNs of 6.92 and 6.69, respectively. A yet different and noteworthy case is represented by the gold-thiolates. The preference of Au(I) for digonal coordination favors the self-assembly of $[Au_n(SR)_{n+1}]^-$ staples, which behave like $R_2P{-}(CH_2)_n{-}PR_2$ diphosphine donors.[26b] This self-reduces the number of CVEs that can be provided by the ligands (four electrons for each *n* of the $[Au_n(SR)_{n+1}]^-$ staple rather than the potential $4(n+1)$) and, accordingly, ends up by favoring polyicosahedral growth of Au frameworks (e.g., $Au_{38}(S{-}CH_2{-}CH_2{-}Ph)_{24}$[10] and $Au_{102}(S{-}p\text{-}C_6H_4{-}COOH)_{44}$[11]).

The study of the chemical and physical properties of **1**, **2**, and **3** is underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files with X-ray crystallographic data for $\mathbf{2}\cdot 2CH_3CN$ and $\mathbf{3}[NEt_4]_5\cdot 3(CH_3)_2CO$; synthesis details for $\mathbf{1}[NEt_4]_5$, **2**, and $\mathbf{3}[NEt_4]_5$; and bond lengths. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: cristina.femoni@unibo.it.

Present Addresses

†Department of Chemistry and James Frank Institute, University of Chicago, Illinois 60637, United States.
‡CNR–Istituto di Scienze e Tecnologie Molecolari, Via C. Golgi 19, 20133 Milan, Italy.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We wish to acknowledge the financial support of University of Bologna and MIUR (PRIN 2008).

■ REFERENCES

(1) Ceriotti, A.; Masciocchi, N.; Macchi, P.; Longoni, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 3724.

(2) Chini, P. *J. Organomet. Chem.* **1980**, *200*, 37.

(3) Femoni, C.; Iapalucci, M. C.; Longoni, G.; Svensson, P. H. *Chem. Commun.* **2004**, 2274.

(4) Femoni, C.; Iapalucci, M. C.; Longoni, G.; Tiozzo, C.; Zacchini, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 6666.

(5) Tran, N. T.; Dahl, L. F. *Angew. Chem., Int. Ed.* **2003**, *42*, 3533.

(6) Mednikov, G.; Dahl, L. F. *Philos. Trans. R. Soc. London, Ser. A* **2010**, *368*, 1301.

(7) Tran, N. T.; Powell, D. R.; Dahl, L. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 4121.

(8) Mednikov, G.; Jewell, M. C.; Dahl, L. F. *J. Am. Chem. Soc.* **2007**, *129*, 11619.

(9) Teo, B. K.; Zhang, H.; Shi, X. *J. Am. Chem. Soc.* **1990**, *112*, 8552.

(10) Qian, H.; Eckenhoff, W. T.; Zhu, Y.; Pintauer, T.; Jin, R. *J. Am. Chem. Soc.* **2010**, *132*, 8280.

(11) Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. *Science* **2007**, *318*, 430.

(12) Wei, Q.-H.; Zhang, L.-Y.; Yin, G.-Q.; Shi, L.-X.; Chen, Z.-N. *Organometallics* **2005**, *24*, 3818.

(13) (a) Longoni, G.; Iapalucci, M. C. In *Clusters and Colloids*; Schmid, G., Ed.; VCH: Weinheim, Germany, 1994; pp 91–177. (b) Longoni, G.; Femoni, C.; Iapalucci, M. C.; Zanello, P. In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A.; Raithby, P. R., Eds.; Wiley-VCH: Weinheim, Germany, 1999; Vol.2, pp 1137–1158.

(14) Vidal, J. L.; Schoening, R. C.; Troup, J. M. *Inorg. Chem.* **1981**, *20*, 227.

(15) Collini, D.; Fabrizi De Biani, F.; Dolzhnikov, D. S.; Femoni, C.; Iapalucci, M. C.; Longoni, G.; Tiozzo, C.; Zacchini, S.; Zanello, P. *Inorg. Chem.* **2011**, *50*, 2790.

(16) Martinengo, S.; Ciani, G.; Sironi, A. *J. Am. Chem. Soc.* **1980**, *102*, 7564.

(17) Fumagalli, R.; Martinengo, S.; Bernasconi, G.; Ciani., G.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1997**, *154*, 1450.

(18) Albano, V. G.; Ceriotti, A.; Chini, P.; Ciani, G.; Martinengo, S.; Anker, W. M. *J. Chem. Soc., Chem. Commun.* **1975**, 859.

(19) See Supporting Information (Table S.1).

(20) See Supporting Information (Table S.1).

(21) Keller, E. *Schakal 99*; University of Freiburg: Freiburg im Breisgau, Germany, 1999.

(22) (a) Farges, J.; De Feraudy, M. F.; Raoult, B.; Torchet, G. *Surf. Sci.* **1985**, *156*, 370. (b) Farges, J.; de Feraudy, M. F.; Raoult, B.; Torchet, G. *Adv. Chem. Phys.* **1988**, *70*, 45.

(23) Mednikov, E. G.; Dahl, L. F. *J. Am. Chem. Soc.* **2008**, *130*, 14813.

(24) Tran, N. T.; Kawano, M.; Dahl, L. F. *J. Chem. Soc., Dalton Trans.* **2001**, 2731.

(25) Hogarth, G.; Kabir, S. E.; Nordlander, E. *Dalton Trans.* **2010**, *39*, 6153.

(26) (a) Washecheck, D. M.; Wucherer, E. J.; Dahl, L. F.; Ceriotti, A.; Longoni, G.; Manassero, M.; Sansoni, M.; Chini, P. *J. Am. Chem. Soc.* **1979**, *20*, 6110. (b) Femoni, C.; Iapalucci, M. C.; Longoni, G.; Zacchini, S.; Zarra, S. *J. Am. Chem. Soc.* **2011**, *133*, 2406.

(27) Mingos, D. M. P. *J. Chem. Soc. Chem. Comm.* **1985**, 1352 . Significantly icosahedral Rh clusters, e.g., $[Rh_{12}(\mu_{12}\text{-}Sn)(CO)_{25-27}]^{4-}$[28] display 166–170 CVE, whereas the $[Pt_{13}(CO)_{12}]^{8-}$ contained in $[Pt_{13}(CO)_{12}\{Cd_5(\mu\text{-}Br)_5Br_3(dmf)_2\}_2]^{2-}$[26b] only features 162 CVE.

(28) Femoni, C.; Iapalucci, M. C.; Longoni, G.; Tiozzo, C.; Zacchini, S.; Heaton, B. T.; Iggo, J. A.; Zanello, P.; Fedi, S.; Garland, M. V.; Li, C. *Dalton Trans.* **2009**, 2217.

(29) Nunokawa, K; Ito, M.; Sunahara, T.; Onaka, S.; Ozeki, T.; Chiba, H.; Funahashi, Y.; Masuda, H.; Yonezawa, T.; Nishihara, H.; Nakamoto, M.; Yamamoto, M. *Dalton Trans.* **2005**, 2726.

(30) Roth, D.; Lewis, G. J.; Jiang, X.; Dahl, L. F.; Weaver, M. J. *J. Phys. Chem.* **1992**, *96*, 7219.

(31) Tran, N. T.; Kawano, M.; Powell, D. R.; Dahl, L. F. *J. Chem. Soc., Dalton Trans.* **2000**, 4138.

(32) Kawano, M.; Bacon, J. W.; Campana, C. F.; Winger, B. E.; Dubek, J. D.; Sirchio, S. A.; Scruggs, S. L.; Geiser, U.; Dahl, L. F. *Inorg. Chem.* **2001**, *40*, 2554.

(33) Mednikov, E. G.; Ivanov, S. A.; Dahl, L. F. *Angew. Chem., Int. Ed.* **2003**, *42*, 323.

(34) Femoni, C.; Iapalucci, M. C.; Longoni, G.; Svensson, P. H.; Wolowska, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 1635.