lene) stainless-steel pressure vessel (fill factor 75%). The reagents were heated at 170°C for 5 d, and then the mixture was slowly cooled to room temperature. The pH value did not show any appreciable change during the hydrothermal reaction. Small, well-formed, green single crystals were formed. Elemental analysis calcd for $C_2H_{11}CrF_3N_2O_3P$: C 9.5, H 4.3, N 11.1, P 12.2, Cr 20.5, F 22.5; found: C 9.3, H 4.1, N 10.8, P 12.0, Cr 20.1, F 22.0. The IR spectrum does not show any bands above 3500 cm^{-1}, in accordance with the absence of $(OH)^-$ groups.[8] A density of 2.11(1) $g\,cm^{-3}$ was measured by flotation in $CHCl_3/CHBr_3$ (60/40).

Physical measurements: The diffuse reflectance spectrum was recorded at room temperature on a Cary 2415 spectrometer from 210–2000 nm. Magnetic measurements on powdered samples were performed at temperatures between 5.0–300 K, using a Quantum Design MPMS-7 SQUID magnetometer. The magnetic field was 0.1 T, a value in the range of linear dependence of magnetization vs. magnetic field, even at 5.0 K.

Structure determination of $(C_2H_{10}N_2)[Cr(HPO_3)F_3]$: $0.08\times0.035\times0.03$ mm, $M_r=251.10$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a=12.801(2)$, $b=9.337(1)$, $c=6.508(1)$ Å, $V=777.9(2)$ Å^3, $Z=4$, $\mu=1.703$ mm^{-1}, $\rho_{calcd}=2.144$ $g\,cm^{-3}$, $F(000)=508$. The data were collected on a BRUKER SMART-APEX CCD automated diffractometer (graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda=0.71073$ Å, $T=100$ K). Of 4588 measured reflections ($2.70°\leq\theta\leq28.45°$), 1176 were independent ($R_{int}=0.0521$) and 1100 observed ($I>2\sigma(I)$). An absorption correction based on symmetry-equivalent reflections was applied using SADABS.[9] The structure was solved by direct methods (SHELXS 97)[10] and refined by the full-matrix least-squares method based on F^2, using the SHELXL 97 computer program[11] belonging to the WINGX V1.63.02 software package.[12] All non-hydrogen atoms were assigned anisotropic thermal parameters. The atomic coordinates of the hydrogen atoms of the phosphite anions were calculated from difference Fourier maps, the hydrogen atoms of the ethylenediammonium cations were geometrically placed. Final R factors: $R1=0.088$ (all data), $wR2=0.127$; max./min. electron density 0.673/−0.976 $e\,Å^{-3}$; goodness of fit on F^2: 0.879. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-412497. A simulation based on the single-crystal structure of $(C_2H_{10}N_2)[Cr(HPO_3)F_3]$ was in excellent agreement with the X-ray powder data, indicating phase purity and high crystallinity.

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Tuning Electronic Behavior of Carbonyl Metal Clusters by Substitution of Interstitial and Capping Atoms**

Davide Collini, Cristina Femoni,
Maria Carmela Iapalucci, Giuliano Longoni,*
Per H. Svensson, and Piero Zanello

Ligand-stabilized, nanosized metal clusters have been proposed as an ultimate solution for nanolithography and microelectronics.[1] In this context metal carbonyl clusters could also play a role as they are potential nanocapacitors. However, for the cluster to truly function as a capacitor, its CO shell should effectively insulate the metal core, and it should be able to reversibly accept and donate electrons. At present there is no evidence of intermolecular exchange of electrons between differently charged carbonyl clusters, at least on the EPR timescale. They act as quantum dots, in which the cluster valence electrons are confined.[2] However, most metal carbonyl clusters displaying redox behavior have fortuitously been obtained.[3]

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[*] Prof. G. Longoni, Dr. D. Collini, Dr. C. Femoni, Prof. M. C. Iapalucci, Dr. P. H. Svensson
Dipartimento di Chimica Fisica ed Inorganica
viale Risorgimento 4, 40136 Bologna (Italy)
Fax: (+39)051-209-3690
E-mail: longoni@ms.fci.unibo.it

Prof. P. Zanello
Dipartimento di Chimica
via Aldo Moro, 53100 Siena (Italy)

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To develop clusters as molecular capacitors, it would be desirable to know how to tailor their geometry and composition in order to modulate their electronic behavior and tune their redox potentials. Complementary work carried out by Dahl and co-workers[4] and our research groups[5] on non-centered icosahedral $Ni_{10}E_2$ and Ni-centered $Ni_{10}E_2(\mu_{12}\text{-Ni})$ carbonyl clusters (E = Ge, Sn, P, As, Sb, Bi, Se, Te) showed that the presence of an interstitial Ni atom alters the number of cluster valence electrons and triggers reversible redox behavior and multivalence in otherwise electron-precise clusters.[5] Therefore, it appeared possible that substitution of the interstitial atom of a given cluster could allow modulation of its electronic behavior. To prove this assumption, we started a systematic investigation of bimetallic Ni–Rh carbonyl clusters with the aim of obtaining body-centered cubic clusters related to either $[Rh_{14}(CO)_{25}]^{4-}$ (**1**)[6] or $[Rh_{15}(CO)_{30}]^{3-}$,[7] but featuring Ni as the interstitial atom. Previously reported Ni–Rh carbonyl clusters—for example, $[Ni_{10}Rh(CO)_{19}]^{3-}$, $[Ni_9Rh_3(CO)_{21}]^{3-}$, $[Ni_6Rh_3(CO)_{17}]^{3-}$, and $[Ni_6Rh_5(CO)_{21}]^{3-}$ [8,9]—were obtained by reaction of $[Ni_6(CO)_{12}]^{2-}$ with 0.25–1 equiv of $[\{Rh(cod)Cl\}_2]$ (cod = cyclooctadiene) or $[\{Rh(CO)_2Cl\}_2]$.

We now report that the addition of 1.5–1.7 equiv of $[\{Rh(cod)Cl\}_2]$ to $[Ni_6(CO)_{12}]^{2-}$ in acetone leads to a mixture of $[NiRh_{13}(CO)_{25}]^{5-}$ (**2**), $[Ni_2Rh_{12}(CO)_{25}]^{4-}$ (**3**), and $[Ni_5Rh_9(CO)_{25}]^{3-}$ (**4**). Owing to similar solubilities of the $[NEt_4]^+$ salts, the complexes were roughly separated by subsequent extractions with acetone. Monitoring by IR spectroscopy indicated that the initial extraction portions contained **4** as the prevalent species, whereas the final portions gave mainly a mixture of **2** and **3**. Upon precipitation with hexane, pure $[NEt_4]_3$[**4**] (30–35% yield based on rhodium) crystallized from the first fraction, and cocrystallized mixtures (20–25% yield) of $[NEt_4]_5$[**2**]) and $[NEt_4]_4$[**3**] separated from the second fraction (see the Experimental Section).

These new tetradecanuclear bimetallic Ni–Rh clusters were shown by X-ray diffraction studies[10] to be isostructural with **1**. In Figure 1 we present the structure of **4** as an example. The major differences between **2**–**4** and **1** (Table 1) are a shrinkage of the central Rh_8 cube, which contains an interstitial Ni atom in **2**–**4** rather than a Rh atom, and a shortening of the M–M interactions involving Ni or the disordered Ni/Rh cap (see below). In detail the four side caps of **4**, which are related by an idealized C_4 axis, are orderly occupied by Ni atoms, whereas the unique cap contained within the C_4 axis is made up of Rh. In contrast, in the cocrystallized mixture of **2** and **3** all the caps of the Ni-centered Rh_8 cube are made up of Rh atoms with the exception of one side cap, whose electron density could be refined as arising from substitutionally disordered Ni/Rh atoms (0.35/0.65, that is, Ni could substitute Rh in some molecules). Accordingly, the unit cell of the cocrystallized mixture contains five $[NEt_4]^+$ cations; however, one cation shows a refined occupancy fraction of 0.65, evidently because it is unnecessary when the cap in question is Ni. Monitoring of several single crystals from different preparations by IR spectroscopy and ESI mass spectrometry confirmed the above result by showing the presence of both **2** and **3** in each examined crystal.

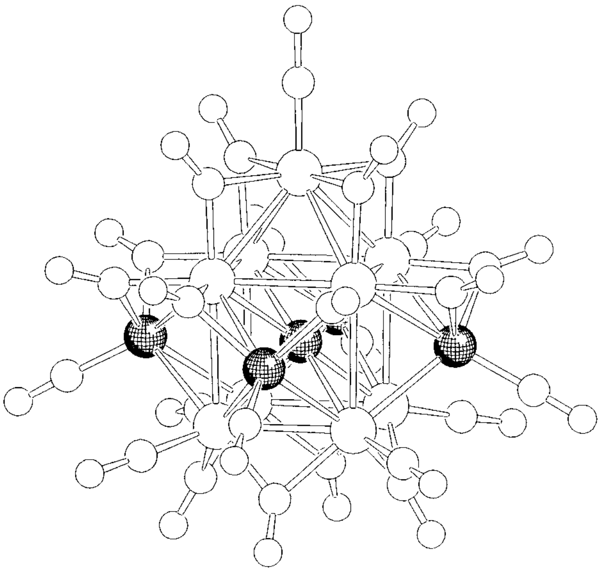

Figure 1. Crystal structure of **4**, as an example of the isostructural clusters **1**–**5**.

Table 1. Selected average M–M distances [Å] in complexes **1**, **2**/**3**, **4**, and **5** (M = Ni, Rh).[a]

	1	**2**/**3**	**4**	**5**
$M_{interstitial}{-}Rh_{cube}$	2.64	2.53	2.49	2.46
$M_{interstitial}{-}Rh_{top\ cap}$	3.38	3.43	3.37	3.39
$M_{interstitial}{-}M_{side\ cap}$	3.08	3.34	3.15	3.13
$Rh{-}Rh_{cube\ (top\ square)}$	3.00	2.95	2.90	2.88
$Rh{-}Rh_{cube\ (bottom\ square)}$	2.80	2.82	2.80	2.75
$Rh{-}Rh_{cube\ (intersquare)}$	3.32	2.99	2.92	2.88
$Rh_{top\ cap}{-}Rh_{cube}$	2.79	2.85	2.84	2.84
$M_{side\ cap}{-}Rh_{cube}$	2.74	2.83	2.67	2.65
$Ni/Rh_{side\ cap}{-}Rh_{cube}$		2.77		

[a] Data for **1** are taken from reference [6d].

A substitution of Rh with Ni that is limited to the side caps of **1** is in keeping with the lower degree of CO coordination at these sites with respect to the top cap. On the contrary, it may appear surprising that Ni could replace Rh as the interstitial atom in the architecture of **1**. Indeed, Ni possesses a lower heat of atomization than Rh[13] and the Ni–CO bond is energetic.[14] Probably, the M–M energy loss upon Ni-centering of a $Rh_{14-x}Ni_x$ cluster is overcome by the gain in energy of the remaining Rh–Rh interactions arising from the contraction of the Rh_8 cube, as well as from substitution of Ni–CO with Rh–CO interactions.

The most striking feature of compounds **1**–**4** is that they are isostructural but not isoelectronic. Figure 2 presents the EHMO diagrams of the frontier region of **1**–**4** obtained with CACAO.[15] These show that two additional MOs (which for **1** are relatively high in energy and fall in the antibonding region) are progressively stabilized as the interstitial Rh and then the side caps are replaced by Ni atoms.

Compounds **1**–**4** display electrochemically reversible redox properties. In particular, **4** can be chemically or electrochemically oxidized in reversible steps to the corresponding congeners $[Ni_5Rh_9(CO)_{25}]^{2-}$ (**5**, $E_{1/2} = -0.34$ V) and $[Ni_5Rh_9(CO)_{25}]^{-}$ (**6**, $E_{1/2} = -0.18$ V). Complex $[NEt_4]_2$[**5**]

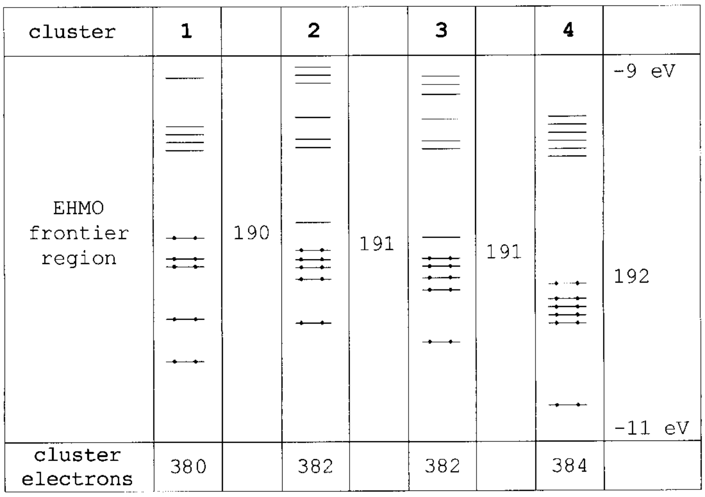

Figure 2. The frontier region between −11 and −9 eV of the EHMO diagram of **1**–**4**. The number of cluster electrons is obtained with the following formula: $N_{\mathrm{Ni}} \times 10 + N_{\mathrm{Rh}} \times 9 + N_{\mathrm{CO}} \times 10 + N_{\text{negative charges}}$

($\tilde{\nu}_{\mathrm{CO}}$ (MeCN) = 2027 s, 1984 m, 1895 m, 1868 s cm^{-1}; $g = 2.07$) has been isolated and characterized by X-ray structure analysis.[10c] As expected, **5** is isostructural with **4**, with the major difference being a further contraction of the Rh_8 cube (see Table 1).

In contrast to complex **1**, compounds **2**–**4** do not readily afford the corresponding hydride derivatives upon protonation. The hydride atom of $[HRh_{14}(CO)_{25}]^{3-}$ is fluxional in solution[16] and swells the Rh_8 cube in the solid state.[6b] Such an effect could justify the lack of propensity for protonation of **2**–**4**, since it would destabilize the observed structures.

In conclusion, **1**–**5** show that progressive Rh/Ni exchange modulates the electronic as well as chemical properties of this cluster architecture and prompts multivalence. As a direct consequence, such an exchange provides a further clue for obtaining more effective molecular capacitors by tailoring the metal cluster composition, as well as for tuning their redox and chemical behavior. This stems from the fact that, in contrast to the situation for main group elements,[17] interstitial metal atoms should not only be regarded as an internal source of electrons. As a function of the relative energies of their valence orbitals, they may alter the number of cluster valence MOs.

Experimental Section

$[NEt_4]_2[Ni_6(CO)_{12}]$ (2.08 g, 2.19 mmol) was dissolved in anhydrous THF (50 mL) in a 250-mL flask under a nitrogen atmosphere. $[\{Rh(cod)Cl\}_2]$ (1.61 g, 3.27 mmol) was added in portions under stirring over a period of 2 h. The resulting brown suspension was dried under vacuum, and the brown precipitate was washed with water (20 mL), THF (20 mL), and methanol (20 mL). The residue was extracted with five portions of acetone (10 mL each). The first two portions were combined, and isopropyl alcohol (30 mL) was diffused into the solution to precipitate 0.59 g of $[NEt_4]_3$[**4**] as black crystals. Elemental analysis calcd for $[NEt_4]_3$[**4**]: Ni 12.71, Rh 40.10, C 25.46, N 1.82, H 2.60; found: Ni 12.4, Rh 40.3, C 25.27, N 1.76, H 2.67; $\tilde{\nu}_{\mathrm{CO}}$ (MeCN) = 2006 s, 1958 m, 1869 m, 1840 s, 1808 cm^{-1}.

The last three portions were also combined and treated to diffusion of isopropyl alcohol (50 mL) to precipitate 0.35 g of a cocrystallized mixture (ca. 2:1) of $[NEt_4]_5$[**2**] ($\tilde{\nu}_{\mathrm{CO}}$ = 1966 s, 1813 cm^{-1}) and $[NEt_4]_4$[**3**] ($\tilde{\nu}_{\mathrm{CO}}$ = 1983 s, 1820 s cm^{-1}). Cyclic voltammetry measurements were performed at a platinum electrode in MeCN containing $[NEt_4]PF_6$ (0.1 mol dm^{-3}) as the supporting electrolyte. The potentials are referred to that of the standard calomel electrode (SCE). Under the present experimental conditions the one-electron oxidation of ferrocene occurs at $E^{\circ\prime} = +0.38$ V.

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direct methods and refined with full-matrix least squares (SHELX97[12]). CCDC-185351 for $[NEt_4]_3[\mathbf{4}]$, CCDC-185352 for $[NEt_4]_2[\mathbf{5}]$, and CCDC-185353 for $0.65[NEt_4]_5[\mathbf{2}]/0.35[NEt_4]_4[\mathbf{3}]$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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Synthesis, X-ray Structure, and Properties of a Tetrabenzannelated 1,2,4,5-Cyclophane**

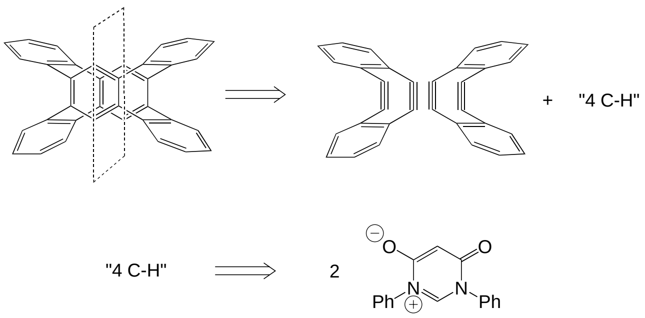
Michael Brettreich, Michael Bendikov,
Sterling Chaffins, Dmitrii F. Perepichka,
Olivier Dautel, Hieu Duong, Roger Helgeson, and
Fred Wudl*

Parylene is the most frequently used material in the protective encapsulation of modern electronic components and medical implants.[1] This high-performance polymer is produced by the pyrolytic decomposition of [2.2]paracyclophane.[1c] Another high-performance organic material with even stronger C–C bonds would be produced if another highly strained, all-aromatic cyclophane could be pyrolyzed, thus resulting in a "superparylene". However, contrary to the mode of pyrolytic decomposition of [2.2]paracyclophane, where scission of the C_{sp^3}–C_{sp^3} bond is the important first step leading to a p-xylylene monomer, in the case of a molecule such as **1** (Scheme 2), cleavage of a biaryl bond would produce a very reactive diradical monomer.

Angle and bond strain in organic molecules and their effect on properties also continue to be an active field of research.[2] Over the last five decades, a substantial number of chemists have prepared many fascinating, strained saturated and unsaturated molecules.[2,3] The most notable of the strained unsaturated molecules are those of the fullerene C_{60}[4] and the cyclophane families.[5] In the former, the hexagons are essentially cyclohexatrienes[6] and in the latter, the hexagons, while considerably distorted, still retain their benzenoid character. Since the first synthesis of [2.2]paracyclophane diene by Dewhirst and Cram,[7] a variety of [2.2]paracyclophanes with unsaturated or benzannelated bridges have been synthesized.[8] The influence of the bridges on the transannular benzene interactions and the geometry of the strained cyclophanes has been widely investigated.[9] To date, only a few unsaturated bridged and benzannelated cyclophanes are known,[9] but no benzannelated $[2_n]$cyclophane with more than two bridges ($n > 2$) has been reported.[10] One would expect that, as the number of *o*-phenylene bridges increased, the total strain would also increase.

To prepare a superparylene and to test the effect of benzo bridges in place of the alkyl bridges of cyclophanes one needs a rapid, reasonably high-yield synthetic entry. A priori, based on existing cyclophane synthetic methodology, the preparation of a symmetrical tetrabenzannelated $[2_n]$cyclophane tetraene would appear to be rather difficult and lengthy. However, careful consideration of the molecular symmetry of the target revealed that the synthesis could be easily achieved. Herein, we describe the synthesis, X-ray structure, and some of the properties of the symmetrically benzannelated $[2_4]$cyclophane tetraene **1**. In future publications we will report on the results of its pyrolytic decomposition.

In Scheme 1 we depict the retrosynthetic analysis with a rather unusual disconnection leading to two dibenzocyclooctadiene-diynes and four methine units. As shown, the latter can originate from a *meso*-ionic precursor.



Scheme 1. Retrosynthetic analysis of **1**.

The synthesis of the tetrabenzocyclophane **1** is based on the known Diels–Alder reactivity of diene **3**[11] to afford **4** (as a mixture of *syn* and *anti* isomers),[12] followed by thermal extrusion of phenyl isocyanate, which leads to a new reactive diene **5** (Scheme 2).[13] The twofold addition of **2**[14] to **3** afforded the bisadduct **4** in 70% yield; the monoadduct does not form even with a 1:1 ratio of reagents. Pyrolysis of **4** gave reactive diene **5** quantitatively. Compound **5** has absorption maxima at 252 and 333 nm, and exhibits a weak blue fluorescence at 406 nm (in THF). It reacts with an excess of

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[*] Prof. F. Wudl, Dr. M. Brettreich, Dr. M. Bendikov, S. Chaffins,
Dr. D. F. Perepichka, Dr. O. Dautel, H. Duong, Dr. R. Helgeson
Department of Chemistry and Biochemistry and Exotic Materials Institute, University of California
Los Angeles, CA 90095-1569 (USA)
Fax: (+1)310-825-0767
E-mail: wudl@chem.ucla.edu

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