Homoleptic Carbonyl Ni–Pd Clusters: Synthesis of $[Ni_{16}Pd_{16}(CO)_{40}]^{4-}$ and $[Ni_{26}Pd_{20}(CO)_{54}]^{6-}$ and Structural Characterization of $[N\mathit{n}Bu_4]_4[Ni_{16}Pd_{16}(CO)_{40}]$**

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Recent collision-induced dissociation studies on the gas-phase $[Pd_3(CO)_6]^-$ cluster[1] supplement other experimental observations,[2–7] which seem to suggest the feasibility of homoleptic carbonylpalladium derivatives. Thus, although the measured average Pd–CO bond dissociation energy (ca. 134 kJ mol^{-1}) is weaker than that measured for the $[Pt_3(CO)_6]^-$ congener (ca. 173 kJ mol^{-1}), its value does not seem, however, sufficient to rule out the possible existence of binary palladium carbonyl compound in solution, unless their formation is hindered by some competing reaction.[1] The belief that the preassembly of a Pd kernel of critical size could ultimately favor the synthesis of a binary palladium carbonyl compound in solution led us to tackle the synthesis of Ni–Pd homoleptic carbonyl bimetallic clusters (HCBCs) as potential precursors of the former. So far, only the related phosphane-substituted derivative $[Ni_9Pd_{33}(CO)_{41}(PPh_3)_6]^{4-}$[8] and the trimetallic derivative $[Au_6Ni_6(Pd_{6-x}Ni_x)Ni_{20}(CO)_{44}]^{6-}$[9] have been reported. To our knowledge, the only Ni–Pd HCBC cited in literature is the incompletely characterized $[Ni_{30-x}Pd_x(CO)_y]^{4-}$ ($x \approx 16$; $y \approx 36$) species, which has been used as precursor for the synthesis of the giant complex $[Pd_{59}(CO)_{32}(PMe_3)_{21}]$.[10]

Investigation of the reaction of $[Ni_6(CO)_{12}]^{2-}$ with Pd^{II} compounds in miscellaneous molar ratios and reaction solvents displayed the existence of wide series of Ni–Pd HCBCs. We report here our first results on the synthesis, chemical properties, and X-ray structurual characterization of the tetraanion $[Ni_{16}Pd_{16}(CO)_{40}]^{4-}$ (**1**), as well as preliminary details of the closely related hexaanion $[Ni_{26}Pd_{20}(CO)_{54}]^{6-}$ (**2**).

The tetrabutylammonium salt of **1** separated out in about 50% yield (based on Pd) as a microcrystalline dark precipitate directly from the reaction of $[N\mathit{n}Bu_4]_2[Ni_6(CO)_{12}]$ with $[Pd(SEt_2)_2Cl_2]$ in THF and was recrystallized by extraction in acetone and precipitation with *n*-hexane. Crystals of $[N\mathit{n}Bu_4]_6[\mathbf{2}]$ were obtained in low yields (5–10%) from the filtered THF reaction solution upon layering with *n*-hexane. The structure of **1**[11] is shown in Figure 1; its metal skeleton is represented in Figure 2 (left) as deriving from condensation of two Ni_8Pd_8 vertex-truncated ν_3-tetrahedra through their Ni_2Pd_5 hexagonal faces, giving rise to a six-layer close-packed metal framework. Two Pd atoms are encapsulated in two Ni_2Pd_{10} twinned cubooctahedral moieties and the cluster surface solely comprises triangular faces with all possible combinations of the two metals. The forty carbonyl groups display most possible CO coordination modes. They comprise linear, and symmetrical edge- and face-bridging ligands, as well as unsymmetrical and semibridging carbonyl groups with sub-van-der-Waals Pd–C contacts of 2.3–2.5 Å. Only nickel atoms bind terminal carbonyl groups. Both homo- and heterometallic edges are spanned by bridging CO groups. Notably, only the Pd_3 triangles of the miscellaneous $Ni_{3-x}Pd_x$

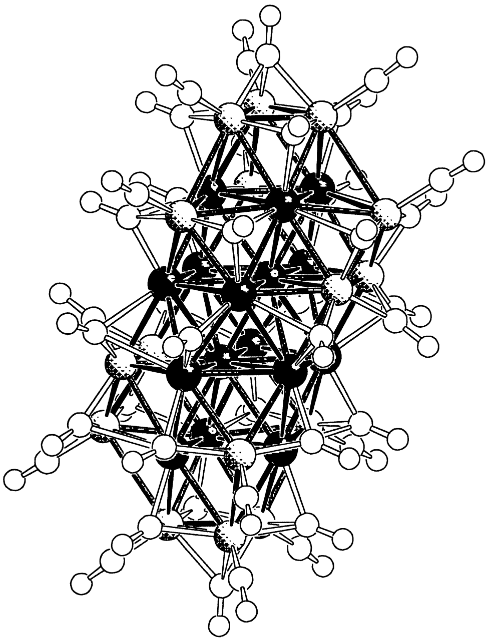

Figure 1. The structure of **1**: black spheres represent the palladium atoms. Range of M–M bonds [Å]: Ni-Ni 2.426(1)–2.473(1), Ni-Pd 2.582(1)–2.825(1), Pd-Pd 2.674(1)–2.930(1). The Ni–Ni inter-layer separations of the outer pair of layers are outside of the above range (mean value 3.07 Å).

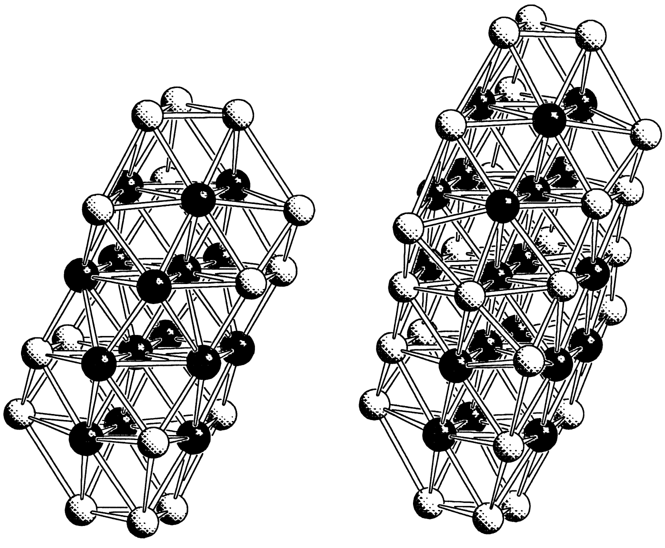

Figure 2. Comparison between the *cp* metal framework of **1** (left; oriented as an *abcbca* sequence of compact layers) and the *ccp* metal framework of **2** (right; as an *abcabca* sequence).

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($x = 0-3$) triangular faces are not capped by a face-bridging carbonyl group. CO binding to Pd only as a bridging ligand in **1** is in keeping with its preferential coordination as a bridging adsorbate on Pd surfaces of different topologies.[15] Such preferential coordination has been explained by a theoretical study.[16]

The HCBC **2**[17] displays a metal structure closely related to that of **1** and a similar carbonyl distribution comprising also capped Pd_3 faces. As shown in Figure 2 (right), its metal framework formally derives by sandwiching a Ni_6Pd_4 layer between the two Ni_8Pd_8 vertex-truncated ν_3-tetrahedra and addition of four capping Ni atoms. As a result, four Pd atoms are encapsulated in the cuboöctahedral moieties.

The Ni-decorated palladium kernels of **1** and **2** (Figure 3) bear little structural resemblance with the so far known Ni–Pt HCBCs, namely $[H_{4-n}Ni_9Pt_3(CO)_{21}]^{n-}$ ($n = 2-4$), $[Ni_{36}Pt_4(CO)_{45}]^{6-}$, and $[H_{6-n}Ni_{38}Pt_6(CO)_{48}]^{n-}$ ($n = 4-6$).[18] The only similarity is shown by the metal atoms of the Ni_6Pd_3 outer moieties, which are arranged as the related moieties of $[H_{4-n}Ni_9Pt_3(CO)_{21}]^{n-}$.

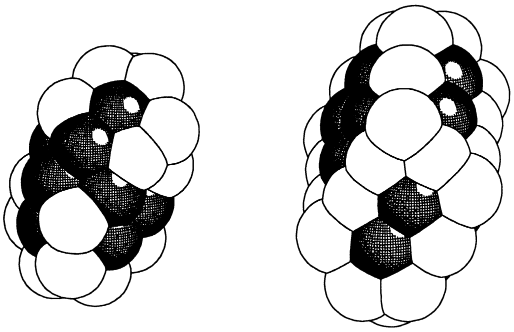

Figure 3. Space-filling model of the nickel-decorated Pd frameworks of **1** (left) and **2** (right).

Extended Hückel(EH) MO calculations with the CACAO program[19] on **1** and **2** disclose neat energy gaps after the 360th and 500th (from bottom) molecular orbitals, respectively. The four and six additional valence electrons, respectively, present in **1** and **2**, populate closely spaced weakly antibonding molecular orbitals delocalized over the inner metal core and carbonyl ligands. The nature of the frontier orbitals and the energy separations between them suggest that **1** and **2** could have several valence electrons and be magnetic.[20, 21] However, preliminary magnetic measurements at room temperature with the Gouy method did not substantiate the presence of unpaired electrons in **1** and **2**.

Both **1** and **2** readily eliminate $Ni(CO)_4$ under a carbon monoxide atmosphere and afford unstable species that contain insignificant amounts of nickel; their solutions display IR patterns almost coincident with those of the smallest carbonylated crystalline Pd/poly(vinylpyrrolidone) colloids,[22] and absorption wavenumbers influenced by their redox state (terminal and bridging CO in the 2040–1990 (mw) and 1930–1890 (s) cm^{-1} range, respectively). If nothing more, the Ni–Pd HCBC may turn out to be possible precursors of palladium carbonyl colloids of tailored size.

Experimental Section

$[Pd(SEt_2)_2Cl_2]$ (1.80 g, 5.04 mmol) was added in portions to a solution of $[NnBu_4]_2[Ni_6(CO)_{12}]$ (3.54 g, 3.02 mmol) in THF (60 mL) under stirring over a period of 6 h. The mixture was left to react for 12 h. The resulting dark brown suspension was filtered. The microcrystalline precipitate was thoroughly washed with water (40 mL) and THF (40 mL), extracted in acetone (40 mL), and precipitated by layering of n-hexane (60 mL) to give black prisms of $[NnBu_4]_4$[**1**] (743 mg, 49.8% based on Pd). The salt is soluble in acetone, acetonitrile, dimethylformamide, and dimethyl sulfoxide, sparingly soluble or insoluble in THF, alcohols, and nonpolar solvents. IR (acetonitrile): $\tilde{\nu}_{CO} = 2016$ (s), 1883 (m), and 1820 (m) cm^{-1}.

Layering of n-hexane on the filtered THF reaction solution afforded black crystals of $[NnBu_4]_6[\mathbf{2}] \cdot x\,C_6H_{14}$ (94 mg). The salt is soluble in acetone, acetonitrile, dimethylformamide, and dimethyl sulfoxide, sparingly soluble in THF, and insoluble in alcohols and nonpolar solvents. IR: (acetonitrile): $\tilde{\nu}_{CO} = 2015$ (s), 1863 (ms), and 1800 (w) cm^{-1}.

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[1] V. A. Spasov, K. M. Ervin, *J. Chem. Phys.* **1998**, *109*, 5344.

[2] Unlike nickel and platinum, palladium carbonyl complexes in solution have only been obtained with ancillary ligands.[3] $Pd(CO)_4$ has been prepared in cryogenic matrices and decomposes upon warming.[4] However, Pd islands grown on alumina[5] and single-crystal Pd surfaces readily adsorb carbon monoxide.[6] Moreover, a purported $[Pd_{13}(CO)_x]$ cluster has been entrapped in a NaY zeolite supercage.[7]

[3] K. R. Dixon, A. C. Dixon in *Comprehensive Organometallic Chemistry II, Vol. 9* (Ed.: R. J. Puddephatt), Pergamon, London, **1995**, p. 198.

[4] E. P. Kundig, D. McIntosh, M. Moskovits, G. A. Ozin, *J. Am. Chem. Soc.* **1973**, *95*, 7234.

[5] J. Libuda, A. Sandell, M. Baumer, H.-J. Freund, *Chem. Phys. Lett.* **1995**, *240*, 429.

[6] Y. Y. Yeo, L. Vattuone, D. A. King, *J. Chem. Phys.* **1997**, *106*, 1990.

[7] L.-L. Sheu, H. Knözinger, W. M. H. Sachtler, *J. Am. Chem. Soc.* **1989**, *111*, 8125.

[8] M. Kawano, J. W. Bacon, C. F. Campana, L. F. Dahl, *J. Am. Chem. Soc.* **1996**, *118*, 7869.

[9] N. T. Tran, M. Kawano, D. R. Powell, R. K. Hayashi, C. F. Campana, L. F. Dahl, *J. Am. Chem. Soc.* **1999**, *121*, 5945.

[10] N. T. Tran, M. Kawano, D. B. Powell, L. F. Dahl, *J. Am. Chem. Soc.* **1998**, *120*, 10986.

[11] Crystal structure analysis data for $[NnBu_4]_4$[**1**], triclinic, space group $P\bar{1}$, $a = 15.9373(15)$, $b = 15.9431(15)$, $c = 17.2319(16)$ Å, $\alpha = 74.692(1)$, $\beta = 73.652(1)$, $\gamma = 79.099(1)^\circ$, $U = 4021.1(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.954$ g cm^{-3}, graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu(Mo_{K\alpha}) = 36.20$ cm^{-1}. A total of 28472 reflections with $1.61^\circ < \theta < 58.60^\circ$ were measured on a Bruker SMART2000 diffractometer at 293 K using a crystal with approximate dimensions $0.25 \times 0.15 \times 0.10$ mm, mounted in air. Data were corrected for Lorentz, polarization, and absorption effects (empirical absorption SADABS[12], transmission factors in the range 0.398–0.696). The structure was solved by direct methods (SIR97[13]) and refined with full-matrix least-squares (SHELX93,[14] 7948 independent reflections having $I > 2\sigma(I)$). All atoms of the anion have been anisotropically refined. Owing to high thermal displacements some C–C distances within the tetrabutylammonium cations are anomalously short. The final R value was 0.0575 ($wR = 0.1545$). Maximum residual electron density -1.19 e Å^{-3}.Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134987. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk)..

[12] G. M. Sheldrick, SADABS, University of Gottingen, Germany, to be published.

[13] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *24*, 435.

[14] G. M. Sheldrick, SHELX93, Program for the Refinement of Crystal Structure, University of Gottingen, Germany, **1993**.

[15] A. M. Bradshaw, F. M. Hoffman, *Surf. Sci.* **1978**, *72*, 513; A. Brown, J. C. Vickerman, *Surf. Sci.* **1983**, *124*, 267; H. Conrad, G. Ertl, J. Koch, E. E. Latta, *Surf. Sci.* **1974**, *43*, 462.

[16] A. B. Anderson, M. K. Awad, *J. Am. Chem. Soc.* **1985**, *107*, 7854.

[17] Crystal structure analysis data for $[NnBu_4]_6[\mathbf{2}] \cdot x\,C_6H_{14}$, space group $P2(1)/n$, $a = 20.449(4)$, $b = 18.066(4)$, $c = 29.392(6)$ Å, $\beta = 97.659(4)^\circ$, $U = 10762(4)$ Å^3, $Z = 2$. Rapid intensity decay during data collection of all measured crystals was observed. Some terminal carbonyl groups showed anomalous thermal motion, while some *n*-butyl chains of the cations and the clathrated *n*-hexane molecules were partially disordered. The structure could only be refined to an unsatisfactory *R* and *wR* factor of 0.098 and 0.259, respectively.

[18] A. Ceriotti, F. Demartin, G. Longoni, M. Manassero, G. Piva, G. Piro, M. Sansoni, B. T. Heaton, *J. Organomet. Chem.* **1986**, *301*, C5; F. Demartin, C. Femoni, M. C. Iapalucci, G. Longoni, P. Macchi, *Angew. Chem.* **1999**, *111*, 552; *Angew. Chem. Int. Ed.* **1999**, *38*, 531; A. Ceriotti, F. Demartin, G. Longoni, M. Manassero, M. Marchionna, G. Piva, M. Sansoni, *Angew. Chem.* **1985**, *97*, 708; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 696.

[19] C. Mealli, D. M. Proserpio, *J. Chem. Educ.* **1990**, *67*, 399.

[20] G. Longoni, C. Femoni, M. C. Iapalucci, P. Zanello in *Metal Clusters in Chemistry, Vol. 2* (Eds.: P. Braunstein, L. Oro, P. Raithby), WILEY-VCH, Weinheim, **1999**, p. 1137.

[21] F. Fabrizi de Biani, C. Femoni, M. C. Iapalucci, G. Longoni, P. Zanello, A. Ceriotti, *Inorg. Chem.* **1999**, *38*, 3721.

[22] J. S. Bradley, J. M. Millar, E. W. Hill, S. Behal, B. Chaudret, A. Duteil, *Faraday Discuss.* **1991**, *92*, 255.

$[Li(thf)_4]_2^{+}[Ga_{12}(C_{13}H_9)_{10}]^{2-}$: The First Molecular Compound with an Icosahedral Ga_{12} Framework[**]

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Starting from metastable AlX and GaX solutions ($X = Cl$, Br, I), which can be prepared by using a cocondensation method,[1] metalloid clusters such as $Al_7R_6^-$,[2] $Al_{12}R_8^-$,[3] $Al_{77}R_{20}^{2-}$,[4] ($R = N(SiMe_3)_2$) and $Ga_{22}R_8$[5] ($R = Si(SiMe_3)_3$, $Ge(SiMe_3)_3$) have recently been synthesized in metathesis reactions. In contrast, there are only a few examples in which polyhedral species such as $(AlR)_n^{x-}/(GaR)_n^{x-}$ ($x = 0, 1, 2$) have been prepared from AlX/GaX solutions or similar routes. In addition to tetrahedral $(MR)_4$ compounds, for example B_4R_4,[6] $Al_4Cp^*_4$,[7] and $Ga_4[C(SiMe_3)_3]_4$,[8] as icosahedral species for the two lightest elements of Group 13, besides numerous boron compounds, only the following aluminum species have been structurally characterized: $Al_{12}iBu_{12}^{2-}$[9] and $Al_{12}(AlBr_{10}) \cdot 2\,THF$.[10, 11] A corresponding molecular gallium compound is as yet unknown,[12] although there are numerous examples of icosahedral partial structures for gallium in solid-state chemistry.[13] We report here on the first molecular compound with an icosahedral Ga_{12} unit.

A metastable GaBr solution, which was obtained by the simultaneous condensation of the high-temperature molecule GaBr with a toluene/THF mixture, was treated with a fluorenyllithium/toluene solution at −78 °C. Allowing the mixture to warm to room temperature, followed by removal of the solvent in vacuo gave a dark red oil, which was subsequently dissolved in THF. Crystals of $[Li(thf)_4]_2[Ga_{12}(C_{13}H_9)_{10}]$ (**1**) were obtained from the resulting dark red THF solution. The result of an X-ray crystal structure analysis of the anionic Ga_{12} unit is shown in Figure 1.

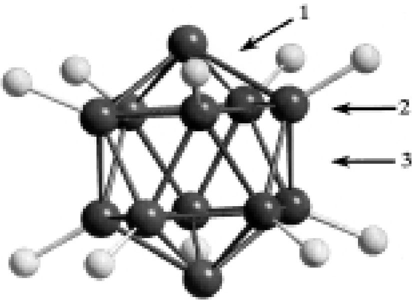

Figure 1. Molecular structure of $Ga_{12}(C_{13}H_9)_{10}^{2-}$ in **1**: For clarity only the carbon atom directly bound to the gallium atom is shown in each case for the fluorenyl ligands. Bond lengths (min./av/max.) [pm] in the different regions labeled by numbered arrows: $d(Ga{-}Ga)_1 = 264.72(7)/265.3/265.87(7)$, $d(Ga{-}Ga)_2 = 258.27(7)/258.9/259.14(6)$, $d(Ga{-}Ga)_3 = 267.33(9)/268.4/269.69(8)$.

The structure reveals that fluorenyl ligands are only bound to ten of the twelve gallium atoms, which are arranged in the form of an icosahedron. This iscosahedron is slightly elongated in the direction of the "naked" gallium atoms, thus the longest Ga−Ga contacts (268.4 pm) are found between the two Ga_5 rings. The distances between the "naked" Ga atoms and the Ga atoms of the respective Ga_5 rings (265.3 pm) are only slightly shorter. The shortest Ga−Ga distances (258.9 pm) of the Ga_{12} framework are found in the Ga_5 rings. The ten fluorenyl ligands are each bound to one gallium atom (205.9 pm) in a σ-like fashion and are tilted in a regular fashion in one direction, which is particularly evident on inspection of **1** along an axis running through the two "naked" Ga atoms (Figure 2).

Since the question of whether the "naked" Ga atoms are each saturated by a H atom could not be answered unambiguously from the X-ray structure analysis, we recorded IR spectra on the crystals; however, these revealed no indications of a Ga−H bond. These experimental findings were confirmed by quantum-chemical calculations,[14] which showed that the Ga−Ga and Ga−C distances calculated for the model compound $Ga_{12}(CH_3)_{10}^{2-}$ are in good agreement with those measured in **1**.[12]

In order to compare the bonding in **1** with the Wade-like bonding in polyhedral boranes by using simple MO diagrams, we performed additional density functional theory (DFT) calculations for $Ga_{12}H_{12}^{2-}$ (**1a**), $Ga_{12}H_{10}^{2-}$ (**1b**), $B_{12}H_{12}^{2-}$ (**1a′**),

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