Synthesis and X-Ray Structure of $[Ni_{16}(CO)_{23}C_4]^{4-}$: a Tetracarbide Anionic Cluster containing Two Interstitial C_2 Fragments

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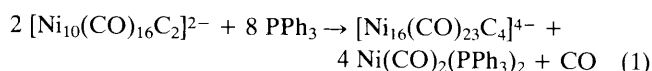
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Reaction of $[Ni_{10}(CO)_{16}C_2]^{2-}$ with four equivalents of PPh_3 in tetrahydrofuran quantitatively afforded the novel brown $[Ni_{16}(CO)_{23}C_4]^{4-}$ tetra-anion, whose metal frame has been shown by X-ray diffraction studies to consist of a unique hexadecanuclear truncated ν_2-octahedron caging two interstitial C_2 moieties with a very short interatomic C–C separation of 1.38 Å.

An investigation of the chemical behaviour of $[Ni_{10}(CO)_{16}C_2]^{2-}$ [1] has resulted in the synthesis and characterization of the $[Ni_{16}(CO)_{23}C_4]^{4-}$ tetra-carbide carbonyl tetra-anion. To our knowledge this represents the first example of a molecular carbonyl cluster interstitially caging more than two carbide atoms[2—6] and shows that the presence in the metal frame of an increasing number of interstitial carbide atoms stabilizes higher nuclearity carbonyl nickel clusters.[7,8]

Several salts of the novel brown $[Ni_{16}(CO)_{23}C_4]^{4-}$ tetra-

anion were quantitatively obtained by reaction of $[Ni_{10}(CO)_{16}C_2]^{2-}$ with triphenylphosphine in tetrahydrofuran (THF) according to equation (1). Reaction of phosphine ligands with metal carbonyl anions generally results either in carbonyl substitution reactions[9] or disproportionation-
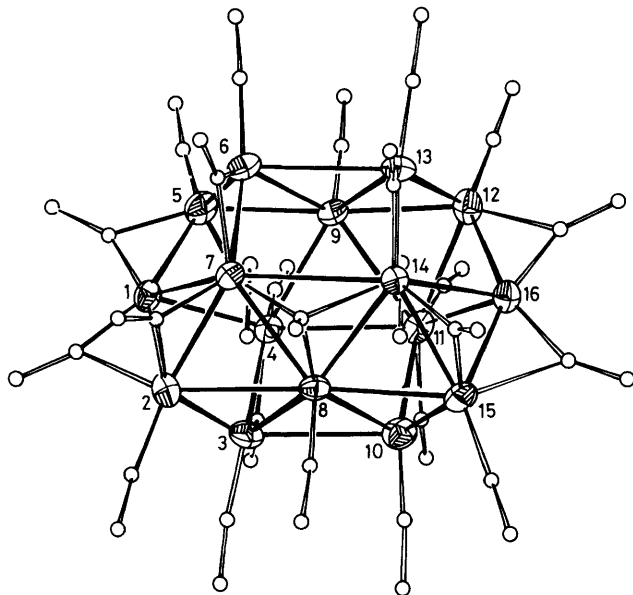
$$2\,[Ni_{10}(CO)_{16}C_2]^{2-} + 8\,PPh_3 \rightarrow [Ni_{16}(CO)_{23}C_4]^{4-} +$$
$$4\,Ni(CO)_2(PPh_3)_2 + CO \quad (1)$$

Figure 1. An ORTEP drawing of the structure of the $[Ni_{16}(CO)_{12}$-$(\mu_2$-$CO)_{10}(\mu_3$-$CO)(C_2)_2]^{4-}$ tetra-anion.

mal parameters for the 86 non-hydrogen atoms has progressed to R 0.065 and R_w 0.077.‡

The structure of the $[Ni_{16}(CO)_{12}(\mu_2$-$CO)_{10}(\mu_3$-$CO)$-$(C_2)_2]^{4-}$ tetra-anion is shown in Figure 1. The metal frame is based on a truncated and distorted ν_2-octahedron of idealized C_{2h} symmetry (the C_2 axis comprises nickel atoms 1 and 16), in which the central nickel atom is missing. The Ni–Ni bond distances are scattered in the range 2.355—3.028 Å, with an overall average value of 2.604 Å. The carbonyl groups reduce the idealized symmetry of the anion to C_s; in addition to a unique face bridging carbonyl group [Ni–C$_{av.}$ 2.015, C–O 1.21(2) Å], there are present 12 terminal (Ni–C$_{av.}$ 1.667, C–O$_{av.}$ 1.200 Å) and 10 edge-bridging ligands (Ni–C$_{av.}$ 1.860, C–O$_{av.}$ 1.215 Å).

The unique and large cavity of this metallic polyhedron is occupied by four interstitial carbide atoms linked in pairs. Within each pair the C–C interatomic separation (av. 1.38 Å) is the shortest found in related moieties;[1—6] between the two pairs the C · · · C interatomic separation is unequivocally non-bonding and shows a mean value of 2.88 Å. The Ni–C (carbide) interactions are in the range 1.935—2.176 Å and have an average value (2.07 Å) almost coincident with that found in $[Ni_{10}(CO)_{16}C_2]^{2-}$.[1] It is worth noting that the whole structure of $[Ni_{16}(CO)_{23}C_4]^{4-}$ (i.e. the metal frame geometry and the stereochemistry of the carbide atoms and most carbonyl ligands) may be envisaged to be derived from fusion of two $[Ni_{10}(CO)_{16}C_2]^{2-}$ moieties[1] and loss of the unique interstitial nickel atom.

To our knowledge the only previously reported tetracarbide clusters are the quasi-molecular bi-octahedral $Gd_{10}Cl_{18}(C_2)_2$ and $Gd_{10}Cl_{17}(C_2)_2$ sub-units, which encapsulate a C_2 moiety (C–C 1.47 Å) in each octahedral cavity.[11]

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induced degradation.[10] The disproportionation-induced condensation represented by equation (1) is unusual, and probably occurs because of the unstable nature of the degradation products of $[Ni_{10}(CO)_{16}C_2]^{2-}$. This behaviour was also shown by the readily reversible degradation reactions of the latter under a carbon monoxide atmosphere to $Ni(CO)_4$ and highly reactive, more reduced dicarbide species.

The $[Ni_{16}(CO)_{23}C_4]^{4-}$ tetra-anion, instead of the expected $[Ni_{10}(CO)_{16}C_2]^{2-}$, is the main product of the reaction in acetonitrile solution of $[Ni_6(CO)_{12}]^{2-}$ with C_2Cl_4, when using the $[NMe_4]^+$ counterion (rather than $[PPh_4]^+$ or $[PPN]^+$†),[1] (yields *ca.* 20% based on nickel), and a great dependence of the products of the above reaction on the starting counterion is emerging.

The $[Ni_{16}(CO)_{23}C_4]^{4-}$ salts ($[NMe_4]^+$, $[PPh_4]^+$, and $[PPN]^+$) are sparingly soluble in THF and acetone and were crystallized in acetonitrile by slow diffusion of di-isopropyl ether [ν_{CO} in acetonitrile solution at 1988(vs), 1849(mw), and 1800(sh) cm^{-1}; no ^{1}H n.m.r. signals from δ 20 to -40, other than those due to the cations; analyses agree with the given formulation]. The exact stoicheiometry and structure of $[NMe_4]_4[Ni_{16}(CO)_{23}C_4]$ were established by an X-ray diffraction study.

Crystal Data: $C_{43}H_{48}N_4Ni_{16}O_{23}$, $M = 1928.2$, space group $P2_1/n$, $a = 12.772(4)$, $b = 21.245(5)$, $c = 23.317(9)$ Å, $\beta = 99.73(3)°$, $U = 6236(6)$ Å^3, $Z = 4$, $D_c = 2.05$ g cm^{-3}, $\mu(Mo$-$K_\alpha) = 48.07$ cm^{-1}, $\lambda = 0.71073$ Å. 9162 Intensities were recorded ($\theta_{max.}$ 24°) on an Enraf-Nonius CAD 4 automated diffractometer, of which 2989 having $I>3\sigma(I)$ were corrected for Lorentz polarization and absorption and used for structure solution and refinement. The structure was solved by direct methods and subsequent difference Fourier syntheses. Refinement of scale factors, positional, and ther-

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† $[PPN]^+$ = bis(triphenylphosphine)iminium cation.