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# A New Direct Synthesis for Dicarbide Clusters: Synthesis and Crystal Structure of $[AsPh_4]_2[Ni_{10}(CO)_{16}C_2]$

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Reaction of $[Ni_6(CO)_{12}]^{2-}$ with either $C_2Cl_4$ or $C_2Cl_6$ results in a direct synthesis for the new dicarbide cluster $[Ni_{10}(CO)_{16}C_2]^{2-}$, which has been isolated and structurally characterized as its tetraphenylarsonium salt.

Several homometallic Ru,Co,Rh and heterometallic Co–Ni dicarbide carbonyl clusters are known.[1—8] They were synthesized under pyrolytic conditions {*e.g.* $[Ru_{10}(CO)_{24}C_2]^{2-}$ and $[Co_{11}(CO)_{22}C_2]^{3-}$},[3,4] or through the redox condensation reactions[5] between two mono-carbide subunits in different oxidation states, either preformed {*e.g.* $[Co_6Ni_2(CO)_{16}C_2]^{2-}$},[6] or generated directly *in situ* by partial oxidation of the parent carbide cluster {*e.g.* $Rh_{12}(CO)_{25}C_2$ and $[Rh_{12}(CO)_{24}C_2]^{2-}$}.[7,8] Those showing short interatomic C–C separations[4,6,7] may provide some insight into C–C bond formation.

We report here a new direct synthesis for dicarbide clusters which has been used to synthesize in high yield the first homometallic nickel dicarbide cluster, namely $[Ni_{10}(CO)_{16}C_2]^{2-}$. This new red dianion, which shows the shortest C–C separation (1.40 Å) reported,[1,2] was initially obtained by thermal condensation of $[Ni_9(CO)_{17}C]^{2-}$ in diglyme at 120 °C. However, pyrolysis of $[Ni_9(CO)_{17}C]^{2-}$ is not always reproducible and often afforded the title compound in a mixture with several other products. In contrast, reaction in acetonitrile of $[Ni_6(CO)_{12}]^{2-}$, as its tetraphenylarsonium or bis(triphenylphosphino)iminium (PPN) salt, with perhalogenohydrocarbons such as $C_2Cl_6$ or $C_2Cl_4$, equation (1), selectively affords $[Ni_{10}(CO)_{16}C_2]^{2-}$ with yields up to 60%. This new direct synthesis of a dicarbide cluster is similar to the well known synthesis of carbide clusters *via* reaction of a carbonyl anion with $CCl_4$.[1,9]

$$2[Ni_6(CO)_{12}]^{2-} + C_2Cl_4 \rightarrow [Ni_{10}(CO)_{16}C_2]^{2-} + 4Cl^- + Ni^{2+} + Ni(CO)_4 + 4CO \qquad (1)$$

The red $[Ni_{10}(CO)_{16}C_2]^{2-}$ dianion has been isolated in the solid state by evaporation *in vacuo* of the reaction solution, and washing of the residue with a methanol solution containing *ca.* 5% of the counterion as its chloride. Both the $AsPh_4^+$ and $PPN^+$ salts have been crystallized from tetrahydrofuran (THF)–cyclohexane or acetone–isopropyl alcohol [$\nu_{CO}$ in THF at 2000(s), 1975(ms), 1875(m), and 1820(m) cm$^{-1}$; no $^1$H n.m.r. signal from δ 20 to −40, other than those due to the cations; analyses ($AsPh_4^+$ or $PPN^+$, Ni and CO) agree with the given formulation]. The exact stoicheiometry and structure of $[AsPh_4]_2[Ni_{10}(CO)_{16}C_2]$ were determined by a single-crystal *X*-ray analysis.†

*Crystal data:* $C_{66}H_{40}As_2Ni_{10}O_{16}$, $M$ = 1826.3, monoclinic, space group $P_c$ (No. 7) after refinement, $a$ = 11.762(4), $b$ = 13.404(4), $c$ = 22.948(8) Å, $\beta$ = 113.5(4)°, $U$ = 3317(4) Å$^3$, $Z$ = 2, $D_c$ = 1.828 g cm$^{-3}$; $\mu$(Mo-$K_\alpha$) = 38.39 cm$^{-1}$. 8321 Intensities were recorded ($2\theta_{max.}$ = 48°) on an Enraf-Nonius CAD 4 automated diffractometer, of which 4286 having $I > 2\sigma(I)$ were corrected for Lorentz polarisation and absorption and used for structure solution and refinement. The structure was solved by direct methods and subsequent difference Fourier synthesis. Refinement of scale factors, positional and thermal parameters for the 94 non-hydrogen atoms has progressed to $R$ = 0.042 [$R_w$ = 0.043].

The structure of the $[Ni_{10}(CO)_6(\mu_2\text{-}CO)_{10}C_2]^{2-}$ dianion is shown in Figure 1. The whole dianion displays a $C_{2h}$-$2/m$ idealized symmetry with the mirror plane comprising nickel atoms 1 and 9 and the two interstitial carbon atoms. The metal polyhedron may be seen as being derived from the condensation of two $\mu_4$-Ni (1 and 9) capped trigonal-prisms sharing the common square face defined by nickel atoms 4, 5, 6, and 7. This description relates the title compound to the recently reported $[Co_6Ni_2(CO)_{16}C_2]^{2-}$, whose metal framework may be obtained by loss of the two capping nickel atoms 1 and 9.[6]

The Ni–Ni distances are scattered in a 2.38—3.00 Å range, and may be divided into three sets: the first set comprises the ten edges spanned by bridging carbonyls, and has a mean

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

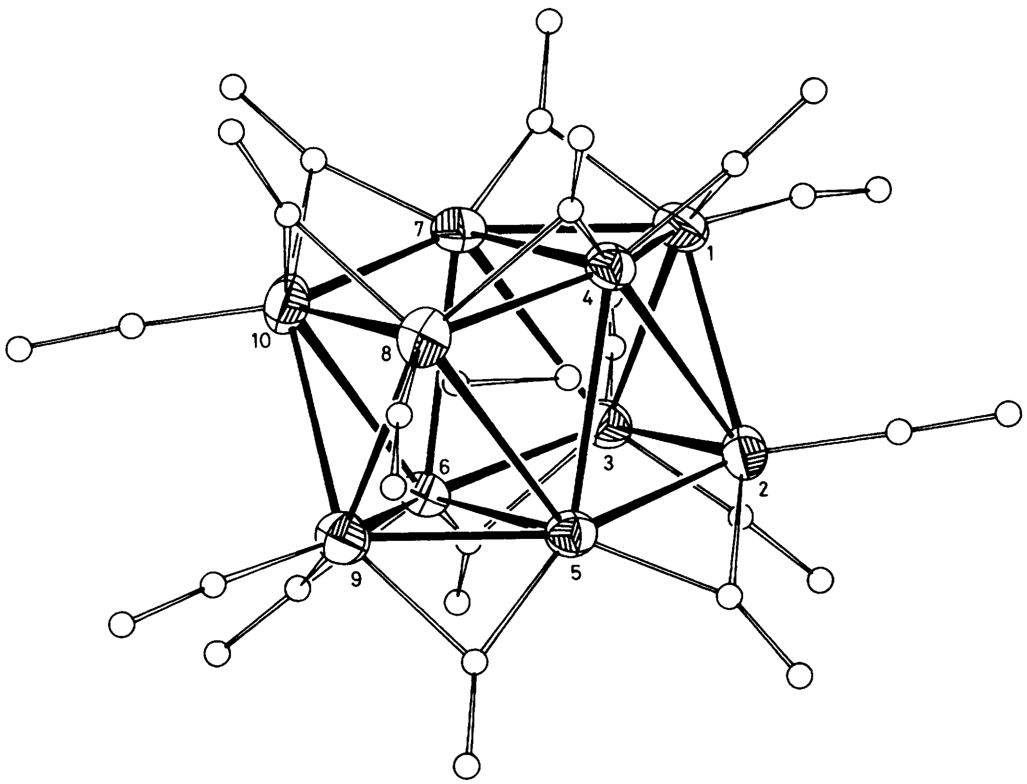

**Figure 1.** The molecular geometry of the $[Ni_{10}(CO)_{16}C_2]^{2-}$ dianion. Ni–Ni bond distances (Å): 1–2 2.645(3), 1–3 2.605(2), 1–4 2.411(2), 1–7 2.399(2), 2–3 2.521(3), 2–4 2.934(3), 2–5 2.401(3), 3–6 2.383(3), 3–7 2.954(3), 4–5 2.849(3), 4–7 2.686(3), 4–8 2.393(3), 5–6 2.699(3), 5–8 2.866(3), 5–9 2.391(3), 6–7 2.892(3), 6–9 2.402(3), 6–10 3.000(3), 7–10 2.398(3), 8–9 2.615(3), 8–10 2.505(3), 9–10 2.640(3).

value of 2.42 Å. The other two sets, each comprising six edges, show average values of 2.65 and 2.92 Å. respectively. The latter 'loose' set is localized in the bi-prismatic central moiety and allows both a closer C–C interaction of 1.40 Å and lodging of each interstitial carbide atom in a larger seven-metal-vertices cage. In nickel carbonyl clusters the preference of carbide atoms for cavities larger than prismatic is already documented for the square-antiprismatic structures of both $[Ni_8(CO)_{16}C]^{2-}$ and $[Ni_9(CO)_{17}C]^{2-}$.[10,11] As a result, it appears conceivable to consider $[Ni_{10}(CO)_{16}C_2]^{2-}$ as a mono-cavity metal cluster encapsulating a $C_2$ fragment. Each carbide atom is co-ordinated to seven nickel atoms with an overall mean interaction of 2.08 Å. Of the sixteen carbonyl ligands six are terminal (Ni–$C_{av.}$ = 1.71 Å) and ten span the ten intra-layer edges non-symmetrically showing mean shorter and longer interactions of 1.82 and 2.06 Å, respectively.

It may be of interest to compare the structure of the previously reported $[Co_3Ni_7(CO)_{15}C_2]^{3-}$[11] and $[Ru_{10}(CO)_{24}C_2]^{2-}$[3] with that of $[Ni_{10}(CO)_{16}C_2]^{2-}$. These three clusters show a closely related metal framework, which may be derived from a bi-octahedral cubic close packed fragment by progressive loosening of one, two, and three bonds, respectively. For instance, the present cluster requires stretching of the Ni–Ni interactions 5–7, 3–5, and 7–8 to the actual values greater than 3.50 Å. As a first approximation it is conceivable that this corresponds to a progressive increase of the number of CVMO's of respectively one, two, and three from the original computed value of $6N+7$.[12] This would allow an electron pair formally available for direct C–C bonding in both $[Co_3Ni_7(CO)_{15}C_2]^{3-}$ and $[Ni_{10}(CO)_{16}C_2]^{2-}$, which, in contrast to $[Ru_{10}(CO)_{24}C_2]^{2-}$, show comparably short C–C interatomic separations.

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