

Synthesis and Structural-bonding Analysis of the $[\text{Ni}_8(\text{PCMe}_3)_2(\text{PMe})_2(\text{CO})_{12}]^n$ Series ($n = 0, 2^-$): Polyhedral Rearrangement of the Electron-precise $(\mu_5\text{-Ni})_2(\mu_4\text{-P})_2$ -Tetracapped Ni_6P_2 Cuneane Framework in the Neutral Parent into an Electron-delocalized Noncentred Ni_8P_4 Icosahedral Cage in the Dianion by a Two-electron Chemical Reduction

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$[\text{Ni}_8(\text{PCMe}_3)_2(\text{PMe})_2(\text{CO})_{12}]$, **1**, which contains a Ni_6P_2 cuneane framework (with a wedge-shaped P–P edge) capped on its two Ni_3P_2 pentagonal faces by nickel atoms and on its two Ni_4 rectangular faces by phosphorus atoms, undergoes a skeletal rearrangement upon a two-electron reduction with K/benzophenone to give the sought-after centrosymmetric $[\text{Ni}_8(\text{PCMe}_3)_2(\text{PMe})_2(\text{CO})_{12}]^{2-}$, **2**, which contains a noncentred pseudo- D_{2h} 1,2,9,12- Ni_8P_4 icosahedral cage; this reduction-induced conversion illustrates the unprecedented geometrical transformation of a 12-vertex tetracapped cuneane polyhedron with 12 skeletal electron pairs into a noncentred 12-vertex icosahedral polyhedron with 13 skeletal electron pairs *via* a diamond–square–diamond (DSD) rearrangement.

The relationship between the structure of a metal cluster and its electron count is of fundamental importance to the understanding of electron-transfer mechanisms, especially in cases in which a redox interconversion of the skeletal framework of a cluster core from one polyhedral arrangement to another has occurred. In this regard, high-nuclearity metal clusters are of particular interest because electron-transfer reactions are sometimes accompanied by dramatic rearrangements of their polyhedral geometries.^{1–5}

As part of our continuing investigation of the physicochemical behaviour of nickel main group carbonyl clusters,^{6–12} we report herein the preparation and structural characterization† of $[\text{Ni}_8(\text{PCMe}_3)_2(\text{PMe})_2(\text{CO})_{12}]$, **1**, and its dianion, **2**, whose structures conclusively show in accordance with electron-counting rules that a noncentred 12-vertex icosahedral polyhedron (*i.e.* a bicapped pentagonal antiprism) can be obtained from the two-electron reduction of a 12-vertex tetracapped cuneane polyhedron in a cluster. This geometrical modification of the tetracapped cuneane Ni_8P_4 core in **1** upon a two-electron reduction, which affords **2** by a localized cleavage of a particular Ni–Ni skeletal bond with concomitant formation of a P–P skeletal bond, emphasizes the importance of electron-counting rules in electronically accounting for (in

the absence of abnormal intramolecular steric interactions) the edge-connectivities observed in a cluster polyhedron.

$[\text{Ni}_8(\text{PCMe}_3)_2(\text{PMe})_2(\text{CO})_{12}]$, **1**, and $[\text{Ni}_8(\text{PCMe}_3)_4(\text{PMe})_2(\text{CO})_8]$, **3**, which has a noncentred $(\mu_4\text{-PR})_6$ -hexacapped octanickel cubic cage, were isolated from the reaction of $[\text{Ni}_{10}(\text{PMe})_2(\text{CO})_{18}]^{2-}$, **4**, and $[\text{Ni}_9(\text{PMe})_3(\text{CO})_{15}]^{2-}$, **5**, with *tert*-butyldichlorophosphine in tetrahydrofuran (THF).‡ The preparation and stereophysical characterization of **4** and **5**,

‡ *Synthesis*: Preparation of $[\text{Ni}_8(\text{PCMe}_3)_2(\text{PMe})_2(\text{CO})_{12}]$, **1**, and $[\text{Ni}_8(\text{PCMe}_3)_4(\text{PMe})_2(\text{CO})_8]$, **3**. In a typical reaction 0.6 ml of 2.5 mol dm^{-3} $\text{P}(\text{CMe}_3)\text{Cl}_2$ solution in THF was added to a THF solution containing 1.02 g of a mixture of **4** and **5** (initial difficulties in separating **4** and **5** have recently been overcome; an investigation of their separate reactivities will be undertaken). The reaction mixture was then stirred at ambient temperature under N_2 for 12 h, after which the solvent was removed under vacuum. Elution of the hexane-soluble extract of the residue on a silica gel column gave the orange-red **3** as the only major product (first band; 25 mg). This air-sensitive compound was unambiguously characterized from an X-ray crystallographic analysis. IR(hexane), ν/cm^{-1} 2005(s); CV (THF) displayed a reversible reduction wave at -1.1 V. Extraction of the remaining reaction residue with toluene gave a dark-brown solution; chromatographic separation (silica gel) resulted in the isolation of *ca.* 45 mg of the air-sensitive green **1**. IR(THF) ν/cm^{-1} ; 2030(s), 1880(mw), 1855(sh). A CV(THF) exhibited two reversible reduction waves (scan rate, 100 mV s^{-1}) with similar relative peak-current heights at $E_{1/2}$ values of -0.37 and -0.58 V (vs. saturated calomel electrode); the assumption of a one-electron process for each reduction wave of **1** is consistent with the chemical reduction and isolation of its dianion, **2**.

Preparation of $[\text{Ni}_8(\text{PCMe}_3)_2(\text{PMe})_2(\text{CO})_{12}]^{2-}$, **2**, as the $[\text{PPh}_4]^+$ salt. Slow addition of a toluene solution of K/benzophenone to a toluene solution of **1** caused the precipitation of a brown-red material; after its dissolution in THF, a solution of $[\text{PPh}_4]\text{Br}$ in 1:1 methanol/distilled, degassed water was added; red crystalline **2** as the $[\text{PPh}_4]^+$ salt was isolated in essentially quantitative yield. This red-brown compound is somewhat soluble in THF and very soluble in acetone or acetonitrile; suitable crystals for an X-ray diffraction analysis were obtained from a layering of diisopropyl ether over an acetone solution. IR (acetonitrile) ν/cm^{-1} ; 1965(s), 1765(mw). A CV (acetonitrile) displayed no reduction waves to -1.5 V and an irreversible oxidation wave at -0.24 V.

† *Crystal data*: X-ray data were obtained at the indicated temperatures using a Siemens diffractometer with Mo-K α radiation. For $[\text{Ni}_8(\text{PCMe}_3)_2(\text{PMe})_2(\text{CO})_{12}]$ ($M = 1074.0$): monoclinic; $P2_1/n$; $a = 9.957(7)$ Å, $b = 11.299(4)$ Å, $c = 15.325(9)$ Å, $\beta = 91.42(5)^\circ$, $V = 1708.4$ Å³; $d_c = 2.09$ g cm^{-3} for $Z = 2$. Anisotropic least-squares refinement (RAELS) converged at $R(F) = 5.90\%$, $R_w(F) = 8.31\%$ for 1345 independent reflections [$I > 3.0\sigma(I)$] obtained at -80°C . Each molecule is centrosymmetrically disordered in the solid state. For $[\text{PPh}_4]^+[\text{Ni}_8(\text{PCMe}_3)_2(\text{PMe})_2(\text{CO})_{12}]^{2-}$ ($M = 1752.8$): monoclinic; $P2_1/n$; $a = 14.120(4)$ Å, $b = 14.568(4)$ Å, $c = 18.643(6)$ Å, $\beta = 111.83(2)^\circ$, $V = 3559.9$ Å³; $d_c = 1.64$ g cm^{-3} for $Z = 2$. Anisotropic least-squares refinement (SHELXTL PLUS) converged with $R(F) = 4.82\%$, $R_w(F) = 6.42\%$ for 5077 independent reflections [$I > 2.5\sigma(I)$] obtained at -80°C . The crystal-ordered dianion has C_i -1 site symmetry. Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

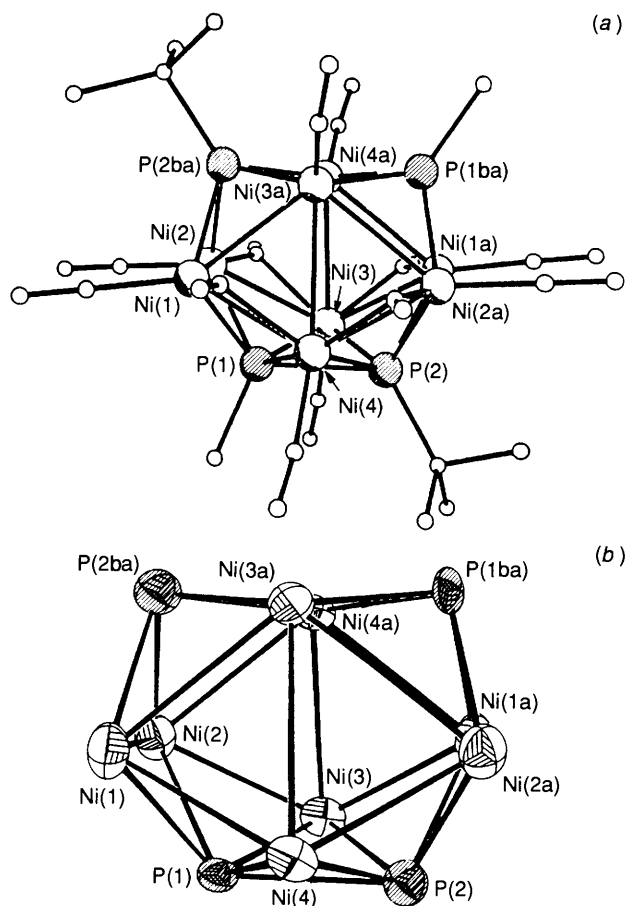


Fig. 1 (a) Molecular configuration of $[\text{Ni}_8(\text{PCMe}_3)_2(\text{PMe})_2(\text{CO})_{12}]$, **1**, which is crystallographically disordered about an averaged centre of symmetry. This molecule, which possesses eight terminal and four doubly bridging carbonyl ligands, has pseudo C_s - m symmetry. (b) The Ni_8P_4 framework of pseudo C_{2v} - $2mm$ symmetry. Its edge-connectivities conform to a Ni_6P_2 cuneane architecture [with P(1) and P(2) forming the 'blade edge' of the cuneane wedge geometry], which is capped on its two Ni_3P_2 pentagonal faces by Ni(3) and Ni(4) and on its two Ni_4 rectangular faces by P(1ba) and P(2ba). The redox-induced geometrical transformation of **1** into **2** involves the breaking of the skeletal edge between Ni(3a) and Ni(4a) of edge-connectivity 6 and the formation of a skeletal edge between P(1ba) and P(2ba) of edge-connectivity 4 such that each nickel and phosphorus atom in the Ni_8P_4 icosahedral cage of **2** has an edge-connectivity of 5.

which contain noncentred 1,12- Ni_{10}P_2 and 1,2,12- Ni_9P_3 icosahedral cages, respectively, with 13 skeletal electron pairs, are presented elsewhere.⁷

Fig. 1 reveals that the idealized C_{2v} configuration of the Ni_8P_4 core of **1** may be viewed as a Ni_6P_2 cuneane architecture (a wedge-shaped eight-vertex structure formed by the fusion of two Ni_3P_2 pentagons along the common P-P edge) which is capped on its two Ni_3P_2 pentagonal faces by nickel atoms and on its two Ni_4 rectangular faces by phosphorus atoms. Each of the eight nickel atoms has an attached terminal carbonyl ligand, while four doubly bridging carbonyl ligands connect the four nickel atoms on the sides of the Ni_6P_2 cuneane polyhedron to the two nickel atoms which cap the pentagonal faces. Inclusion of the Me and CMe_3 substituents, of which each is attached to one of the two tetracapped and two edge-fused P atoms, lowers the pseudo- C_{2v} symmetry of **1** to C_s with the pseudo-mirror plane passing through the four phosphinidene ligands. The formulation of the Ni_6P_2 cuneane framework in **1** as an edge-localized electron-pair polyhedron with 12 skeletal electron pairs is consistent with it being structurally analogous and electronically equivalent to the

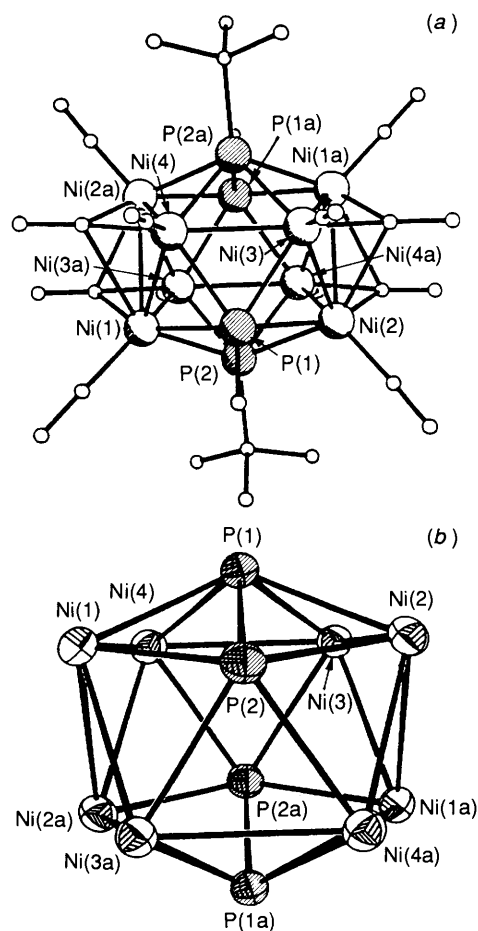


Fig. 2 (a) Configuration of the $[\text{Ni}_8(\text{PCMe}_3)_2(\text{PMe})_2(\text{CO})_{12}]^{2-}$ dianion, **2**, which possesses crystallographic C_i -1 site symmetry. This centrosymmetric crystal-ordered dianion, which has eight terminal and four asymmetrically coordinated triply bridging carbonyl ligands, approximately conforms to C_{2h} - $2/m$ symmetry with the pseudo-mirror plane passing through the four phosphinidene ligands. (b) The 1,2,9,12-tetrasubstituted Ni_8P_4 icosahedral cage of pseudo D_{2h} - mmm symmetry. One mirror plane contains the four phosphorus atoms, while the other two perpendicular mirror planes each contain four nickel atoms.

electron-precise tetracyclic C_{2v} cuneane, C_8H_8 , which was first isolated by Eaton and coworkers¹³ (who coined its name from the Latin 'cuneus', a wedge) from the catalytic isomerization of the O_h valence isomer, cubane.

Since the tetracapped-cuneane Ni_8P_4 polyhedron of **1** has the same number of vertices (12) and edge-connectivities (30) but one less skeletal electron pair than a noncentred icosahedral polyhedron, the chemical reduction of **1** with K/benzophenone was carried out. The desired centrosymmetric $[\text{Ni}_8(\text{PCMe}_3)_2(\text{PMe})_2(\text{CO})_{12}]^{2-}$ dianion, **2**, possessing a noncentred icosahedral Ni_8P_4 cage with 13 skeletal electron pairs was obtained in quantitative yield. This geometrical transformation upon a two-electron reduction of **1** involves the scission of the interpentagonal Ni-Ni skeletal bond (common to both Ni_4 rectangular faces of the cuneane) between the two nickel atoms of edge-connectivity 6 and formation of a P-P skeletal bond between the two phosphorus atoms of edge-connectivity 4 capping the Ni_4 rectangular faces. The resulting centrosymmetric noncentred 1,2,9,12- Ni_8P_4 icosahedral cage in **2** of pseudo- D_{2h} symmetry (Fig. 2) is related to the two icosahedral dianions, **4** and **5**, by the isolobal replacement of a $\text{Ni}(\text{CO})_3$ fragment with an electronically equivalent four-electron donating phosphinidene fragment.

The skeletal rearrangement of **1** into **2** may be described in terms of a diamond-square-diamond (DSD) process in which an edge-connectivity common to two triangular faces of the tetracapped cuneane polyhedron is cleaved and a new edge-connectivity perpendicular to it is formed; DSD mechanisms have been widely used to rationalize fluxional processes and isomerizations of borane, carbaborane, metalloborane, and metal cluster polyhedra.^{14,15}

Especially noteworthy is that cyclic voltammograms (CVs) of **1** exhibit two reversible one-electron reduction waves, whereas a CV of **2** displays an irreversible oxidation wave; these electrochemical data are rationalized in terms of the tetracapped cuneane **1** undergoing rapid reversible electron-transfer reductions to its monoanion and dianion, followed by an irreversible structural transformation to the icosahedral dianion the rate of which is slow relative to the electron-transfer rates. The remarkable geometrical-electronic relationship between the icosahedron and the tetracapped cuneane, suggests the distinct possibility of a tetracapped cuneane as an intermediate or transition state in isomerizations of icosahedral clusters. Further studies of chemical-electrochemical-induced framework interconversions of related icosahedral $\text{Ni}_{12-x}\text{E}_x$ clusters are currently underway.

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