

Condensation of Nickel–Carbonyl Clusters with Soft Lewis Acids: Synthesis and Characterisation of the $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ Dimer

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Reaction of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ in thf with 2 equiv. of the soft Lewis acid $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ gives the new dimeric species $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$. The formation of the latter is not the result of direct addition of CdCl_2 to $[\text{Ni}_6(\text{CO})_{12}]^{2-}$, but it involves some intermediate species, i.e. $[\text{Ni}_9(\text{CO})_{18}]^{2-}$ and $[\text{Ni}_9(\text{CO})_{18}\text{Cd}_2\text{Cl}_4]^{2-}$. The crystal structure of $[\text{NBu}_4]_3\cdot\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}\cdot\text{thf}$ was ascertained by X-ray crystallography. In the solid state, the $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ cluster

anions are pillared along the crystallographic *c* axis, forming infinite columns of perfectly alternating cluster anions and thf molecules. The chemical and electrochemical behaviours of $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ are also reported and compared to those of the parent $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ dianion.

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1. Introduction

Several low-valent metal clusters, stabilised mainly or uniquely by carbonyl ligands, apart from being molecules or molecular ions perfectly defined in composition and all structural details, trespass by size in the field of nanomaterials (1–1000 nm) from the lowest limit.^[1] Pseudo 1D molecular carbonyl clusters (MCC) possessing nanometric size have been known for a long time. For instance, the $[\text{Pt}_{15}(\text{CO})_{30}]^{2-}$ dianion has a metal frame length of ca. 1.5 nm. More-or-less spherical or ellipsoidal clusters, such as $[\text{Ni}_{32}\text{Pt}_{24}(\text{CO})_{56}]^{6-}$,^[3] $[\text{Ni}_{26}\text{Pd}_{20}(\text{CO})_{54}]^{6-}$,^[4] $\text{Pd}_{59}(\text{CO})_{32}(\text{PMe}_3)_{21}$,^[5] $\text{Pd}_{69}(\text{CO})_{36}(\text{PEt}_3)_{18}$,^[6] and the giant three-shell $\text{Pd}_{145}(\text{CO})_x(\text{PEt}_3)_{30}$ ($x \approx 30$),^[7] display metallic core diameters in the 1–2-nm range. Moreover, several MCC aggregates close to or trespassing in the nanofield can be prepared, for instance by the fusion of two or more anionic clusters with a central core constituted by a single cation, for example $\{\text{Hg}[\text{Os}_{10}\text{C}(\text{CO})_{24}]_2\}^{2-}$,^[8] or cationic moieties, such as $[\text{H}_2\text{Ru}_{12}\text{Cu}_6\text{Cl}_2(\text{CO})_{34}]^{2-}$,^[9] $[\text{H}_4\text{Ru}_{20}\text{Cu}_6\text{Cl}_2(\text{CO})_{48}]^{4-}$,^[10] and $[\text{Ag}_3\text{Ru}_{10}\text{C}_2(\text{CO})_{28}\text{Cl}]^{2-}$.^[11] The existence in solution of several fused MCC moieties such as $\{\text{Ag}[\text{Rh}_6\text{C}(\text{CO})_{15}]_2\}^{3-}$ and higher $\{\text{Ag}_{n-1}[\text{Rh}_6\text{C}(\text{CO})_{15}]_n\}^{n-}$ oligomers was demonstrated several years ago by multinuclear NMR spectroscopy,^[12] and envisions the possibility to isolate MCC aggregates well beyond 2 nm. For instance, an

infinite $\{\{\text{AgRu}_6\text{C}(\text{CO})_{16}\}^-\}_\infty$ superwire was quantitatively assembled by the reaction of $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ with Ag^+ ions.^[13] Miscellaneous 1D and 2D arrays assembled through η^2 -carbonyl groups of the previously unknown $[\text{Co}_4(\text{CO})_{11}]^{2-}$ dianion with Yb^{II} or Eu^{II} cations were obtained by the reaction of $\text{Hg}[\text{Co}(\text{CO})_4]_2$ with Yb or Eu metals.^[14]

Recently, we reported two different strategies for the polymerisation of MCC. First, the controlled oxidation of $[\text{Pt}_6(\text{CO})_{12}]^{2-}$ affords the $[\text{Pt}_{18}(\text{CO})_{36}]^{2-}$ and $[\text{Pt}_{24}(\text{CO})_{48}]^{2-}$ dianions that self-assemble by formation of homometallic Pt–Pt bonds into 1D $\{[\text{Pt}_{18}(\text{CO})_{36}]^{2-}\}_\infty$ and $\{[\text{Pt}_{24}(\text{CO})_{48}]^{2-}\}_\infty$ infinite wires upon crystallisation.^[15] Secondly, the reaction of $[\text{NBu}_4]_2[\text{Pt}_9(\text{CO})_{18}]$ with the soft Lewis acid CdCl_2 gives the $[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}$ adduct, which self-assembles upon crystallisation into a 1D $\{[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}\}_\infty$ polymer through the formation of chloride bridges.^[16]

Nickel is known to have a more limited chemistry than platinum for what concerns homometallic carbonyl clusters. For instance, nickel displays only the first two species in the series $[\text{Ni}_{3n}(\text{CO})_{6n}]^{2-}$ ($n = 2, 3$),^[17,18] whereas several compounds were prepared and characterised in the $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n = 2\text{--}10$) series.^[2] Therefore, self-assembly of $[\text{Ni}_{3n}(\text{CO})_{6n}]^{2-}$ ($n = 2, 3$) units into 1D infinite wires seems unlikely owing to excessive electrostatic repulsion between anions, even if $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ in its $[\text{NMe}_4]^+$ salt gives rise to columnar stacks.^[19] For this reason, we focused our attention on the possibility of building-up oligomeric species based on nickel MCC following the second route described above, i.e. the assembly of nickel clusters with Lewis acids. We report here our results on the oligomerisation of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ with the soft Lewis acid CdCl_2 .

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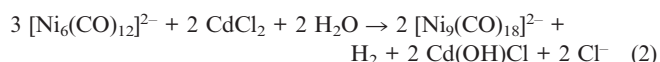
2. Results and Discussion

2.1 Synthesis of $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$

The reaction of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ in thf with 2 equiv. of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ directly affords the $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ oligomer in good yields (ca. 60% based on Ni). The IR spectrum shows $\nu(\text{CO})$ at higher frequencies [2025(vs), 1844(m) and 1819(m) cm^{-1} , in thf] relative to the parent $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ [1980(s), 1810(m) and 1790(m) cm^{-1} , in thf], in agreement with the lower negative charge per $[\text{Ni}_6(\text{CO})_{12}]$ unit. Despite the fact that the formation of $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ could appear to be the result of the addition of CdCl_2 to one triangular face of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ followed by condensation of two of these units and loss of one Cl^- ligand, according to Equation (1), this does not seem to be the case.

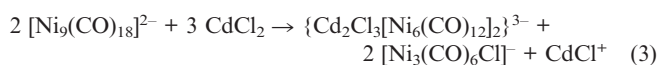


In fact, careful study of the course of the reaction after the addition of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ in small portions to a solution of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ indicates a more complex pathway. The first product formed is, in fact, the previously reported $[\text{Ni}_9(\text{CO})_{18}]^{2-}$ anion,^[17,18] which is the main species present in solution after the addition of ca. 0.5–1 equiv. of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$. The formation of $[\text{Ni}_9(\text{CO})_{18}]^{2-}$ can in principle arise by either the oxidation due to the Cd^{2+}/Cd or the H^+/H_2 redox couple consequent to the Bronsted acidity of the water molecules that are coordinated to Cd^{II} . As detailed below in Section 2.4, the first oxidation of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ irreversibly occurs at -0.22 V, and the oxidation potential is only slightly affected by the solvent and the nature of the electrode. By taking this potential and the standard redox potential in water of the Cd^{2+}/Cd couple (-0.40 V) as very rough references, it may be suggested that reduction of Cd^{II} to Cd^0 by $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ is not thermodynamically favoured. Therefore, the oxidation of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ to $[\text{Ni}_9(\text{CO})_{18}]^{2-}$ can probably be ascribed to the H^+/H_2 redox couple brought about by the acidity of the coordinated water of the $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ salt. Indeed, though the pK_a of the hydrated Cd^{II} ion is relatively high (10.1), it is known that $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ is converted into $[\text{Ni}_9(\text{CO})_{18}]^{2-}$ and $[\text{H}_{4-n}\text{Ni}_{12}(\text{CO})_{21}]^{n-}$ by weak protonic acids and even upon hydrolysis in neutral water.^[20] Considering Equation (2), this process would require 0.67 mol of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ per mole of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$, in fair agreement with our experimental findings.

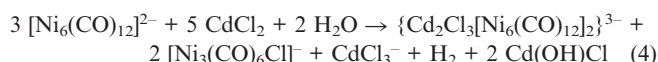


Further addition of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ to the solution results in the formation of a new species that displays $\nu(\text{CO})$ in thf at 2036(vs) and 1824(ms) cm^{-1} . This species could not be isolated and identified, as it was always obtained as a mixture with either $[\text{Ni}_9(\text{CO})_{18}]^{2-}$ or $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$. Nonetheless, considering the fact that this species displays $\nu(\text{CO})$ at higher frequencies relative to both $[\text{Ni}_9(\text{CO})_{18}]^{2-}$ and $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$, we speculatively assume that

it could consist of an adduct between $[\text{Ni}_9(\text{CO})_{18}]^{2-}$ and CdCl_2 , probably featuring a $[\text{Ni}_9(\text{CO})_{18}\text{Cd}_2\text{Cl}_4]^{2-}$ formula. Indeed, the species displays an IR spectrum almost coincident with that of the related $[\text{Pt}_9(\text{CO})_{18}\text{Cd}_2\text{Cl}_4]^{2-}$ species, which was fully characterised.^[16] Further addition of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, reaching the overall Cd/Ni_6 ratio of ca. 2 results in the complete conversion of this adduct into the final $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$. The suggestion that $[\text{Ni}_9(\text{CO})_{18}]^{2-}$ is an intermediate during the formation of $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ was examined by the reaction of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ with a preformed sample of $[\text{Ni}_9(\text{CO})_{18}]^{2-}$ prepared by literature methods.^[17,20] As shown by IR spectroscopic monitoring, this latter reaction occurs with elimination of $\text{Ni}_3(\text{CO})_6$ moieties as $[\text{Ni}_3(\text{CO})_6\text{Cl}]^-$, according to Equation (3). The $[\text{Ni}_3(\text{CO})_6\text{Cl}]^-$ byproduct is very unstable and readily decomposes to Ni, chloride ions and $\text{Ni}(\text{CO})_4$, which is indeed observed as the only carbonyl final byproduct:



The sum of Equations (2) and (3) suggests that the most plausible formal stoichiometry for the formation of $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ requires 1.67 mol of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ per mole of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$, in fair agreement with the experimentally required ratio between the starting materials [Equation (4)].



The fact that Ni carbonyl moieties are partially lost during this process explains why the yields based on Ni are not very high (ca. 60%). By considering the overall Equation (4), in fact, it is possible to conclude that the yield in $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ based on Ni cannot exceed 67%.

2.2 Crystal Structure of $[\text{NBu}_4]_3\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\} \cdot \text{thf}$

The crystal structure of $[\text{NBu}_4]_3\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\} \cdot \text{thf}$ was ascertained by X-ray crystallography. The unit cell contains 6 cluster anions, 18 $[\text{NBu}_4]^+$ cations and 6 thf molecules. Some short contacts (below the sum of the van der Waals radii) exist between the carbonyl ligands of the cluster anions and the C–H groups of the $[\text{NBu}_4]^+$ cations and the thf molecules. Owing to the high symmetry of the $R\bar{3}c$ space group, only one sixth of one $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ anion, one half of $[\text{NBu}_4]^+$ and one thf molecule are independent. Moreover, both $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ and thf lay along the $\bar{3}$ axis, and they display some disorder. In particular, the thf molecule is disordered over six positions, the $[\text{Ni}_3(\text{CO})_6]$ triangle bonded to Cd is disordered over three positions and the bridging Cl ligand is statistically disordered over six positions. All above positions are related by $\bar{3}$ symmetry and give an overall count of three chloride ligands and one thf molecule per cluster anion. As shown in Figure 1, the $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ cluster can be described as being

composed of two $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ units joined by a Cd_2Cl_3^+ bridge. Therefore, $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ can be regarded as a Lewis acid–base adduct between the soft acid Cd_2Cl_3^+ and the soft basic sites of two $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ units, represented by the Ni_3 faces. Regarding the $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ units, these surprisingly display a distorted trigonal prismatic geometry, rather than the usual antiprismatic configuration found in the crystal structure of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$,^[17] and for this it rather resembles the analogous platinum compound $[\text{Pt}_6(\text{CO})_{12}]^{2-}$.^[2,19] As shown in Table 1, which collects the most significant molecular parameters, the intratriangular Ni–Ni distances fall in the narrow range 2.349(6)–2.381(6) Å [average 2.366(10) Å], as previously found in $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ and $[\text{Ni}_9(\text{CO})_{18}]^{2-}$.^[17,18] Conversely, the intertriangular Ni–Ni distances span quite a wide range [2.416(4)–2.712(4) Å], showing also an unusually short contact; by comparison the average intertriangular distances is 2.77 Å in the antiprismatic cluster $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ and 2.766 Å and 2.719 Å for the antiprismatic and prismatic moieties of $[\text{Ni}_9(\text{CO})_{18}]^{2-}$,^[17,18] respectively. The unusually short Ni–Ni intertriangular distances displayed by $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ are due to its distorted trigonal prismatic structure. In particular, the distortion involves the inner triangle, which is slightly shifted and tilted with respect to the outer one, and this explains the very short Ni(1)–Ni(2) distance [2.416(4) Å]. As a consequence of this short bond, the diagonal contact of the corresponding distorted square face of the prism is quite shortened [Ni(2)–Ni(1)#1 2.982(5) Å] relative to the other diagonals [3.171(5)–3.854(4) Å]. Because the centre of the inner $\text{Ni}_3(\text{CO})_6$ triangle is shifted with respect to the symmetry axis in which the Cd atom lies, three different Ni–Cd distances are present in the range 2.656(3)–2.802(4) Å. As far as we are aware, the only example of a structurally characterised molecule containing a Ni–Cd interaction is $\text{Cp}_2\text{Ni}_2\text{Cd}_3(\text{GePh}_3)_4$,^[21] for which the bond lengths are 2.459 and 2.476 Å. The fact that the Ni–Cd bonds in $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ are considerably longer can be explained on the basis of the fact that in the latter the Cd atom is coordinated to a Ni_3 triangle probably by a 4c–2e bond, whereas it is connected to single Ni atoms in $\text{Cp}_2\text{Ni}_2\text{Cd}_3(\text{GePh}_3)_4$.

The Cd_2Cl_3 bridge shows a relatively short Cd–Cd distance [3.236(1) Å]. This contact is shorter than the Cd–Cd distances displayed by other compounds containing the $\text{Cd}_2(\mu\text{-Cl})_3$ group [3.283–3.647 Å],^[22] and even the loosest Cd–Cd contacts in metallic cadmium [3.286 Å]. Direct Cd–Cd bonds in molecular compounds, with distances below the sum of Pauling's single-bond metallic radii for cadmium [2.82 Å], are very rare and, as far as we are aware, the only two species structurally characterised so far are the Cd^{I} derivatives of formula $\text{Ar}'\text{CdCdAr}'$ [$\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_3\text{-2,6-}i\text{Pr}_3)_2$; Cd–Cd 2.6257(5) Å]^[23a] and $[\text{Cd}_2][\text{AlCl}_4]_2$ [Cd–Cd 2.576(1) Å].^[23b] Therefore, even though the Cd–Cd contact in the $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ anion is shorter than that in other $\text{Cd}_2(\mu\text{-Cl})_3$ moieties, its length seems to argue against the presence of a significant direct bonding interaction. It may be speculated that electron donation from the

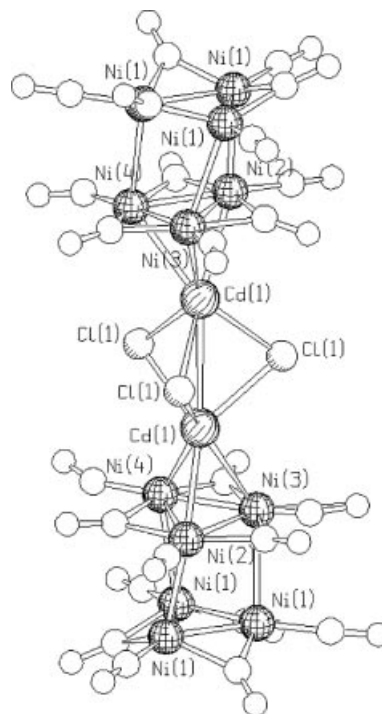


Figure 1. Molecular structure of $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$.

Table 1. Bond lengths [Å] in the $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ cluster anion.

Ni(1)–Ni(1) ^{[a]1}	2.365(2)	Ni(2)–C(8)	1.873(10)
Ni(1)–Ni(2)	2.416(4)	Ni(2)–C(6)	1.874(9)
Ni(1)–Ni(3) ^{[a]2}	2.680(5)	Ni(3)–C(4)	1.756(10)
Ni(1)–Ni(4) ^{[a]1}	2.712(4)	Ni(3)–C(7)	1.862(10)
Ni(2)–Ni(3)	2.349(6)	Ni(3)–C(6)	1.867(10)
Ni(2)–Ni(4)	2.381(6)	Ni(4)–C(5)	1.758(10)
Ni(3)–Ni(4)	2.374(4)	Ni(2)–C(3)	1.767(10)
Ni(2)–Cd(1)	2.656(3)	Ni(4)–C(7)	1.858(10)
Ni(3)–Cd(1)	2.802(4)	Ni(4)–C(8)	1.860(10)
Ni(4)–Cd(1)	2.749(4)	C(1)–O(1)	1.145(8)
Ni(1)–Ni(2) ^{[a]2}	2.982(5)	C(2)–O(2)	1.163(8)
Cd(1)–Cl(1)	2.590(15)	C(3)–O(3)	1.161(10)
Cd(1)–Cl(1) ^{[a]3}	2.597(15)	C(4)–O(4)	1.142(10)
Cd(1)–Cd(1) ^{[a]3}	3.236(1)	C(5)–O(5)	1.140(10)
Ni(1)–C(1)	1.753(11)	C(6)–O(6)	1.166(10)
Ni(1)–C(2)	1.826(11)	C(7)–O(7)	1.145(10)
Ni(1)–C(2) ^{[a]1}	1.931(10)	C(8)–O(8)	1.165(10)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-y + 1, x - y, z$; #2: $-x + y + 1, -x + 1, z$; #3: $y + 1/3, x - 1/3, -z + 13/6$.

$[\text{Ni}_6(\text{CO})_{12}]^{2-}$ units would increase electron density onto the Cd^{II} ions and may shorten the Cd–Cd distance, formally owing to their partial reduction. It is well-known that reduction of Hg^{II} to Hg^{I} results in the formation of a Hg–Hg bond.

The $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ cluster anions are pillared along the crystallographic c axis, forming infinite columns of perfectly alternating cluster anions and thf molecules (Figure 2). Viewing the packing of $[\text{NBu}_4]_3\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\} \cdot \text{thf}$ along the crystallographic c axis (Figure 3) shows a perfect 2D hexagonal arrangements of these infinite columns, which are separated by the $[\text{NBu}_4]^+$ cat-

ions. Moreover, all the consecutive $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\} \cdot \text{thf}$ columns in this 2D arrangement are shifted along the c axis to optimise the crystal packing. The distance between the centroids of the outer $\text{Ni}_3(\text{CO})_6$ triangles of two consecutive $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ cluster anions is 8.338 Å, whereas the analogous separation of the two inner triangles of the same anion is 7.893 Å, suggesting that replacement of the thf molecule with a second Cd_2Cl_3^+ bridge could result in the formation of a perfectly alternated copolymer.



Figure 2. View along the b axis of the crystal packing of $[\text{NBu}_4]_3\text{-}\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\} \cdot \text{thf}$.

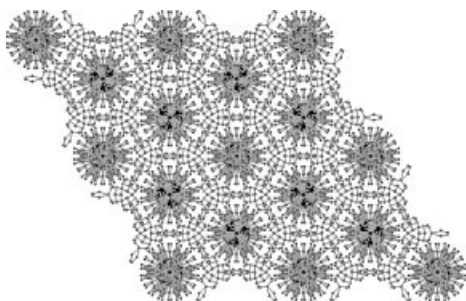


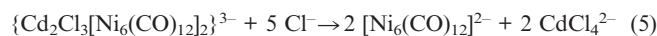
Figure 3. View along the c axis of the crystal packing of $[\text{NBu}_4]_3\text{-}\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\} \cdot \text{thf}$.

2.3. Reactivity of $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$

With the aim to prepare the above-suggested alternating copolymer, the $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ cluster was treated

in thf with excess CdCl_2 , but without any major success, apart from the formation of a small amount of an amorphous precipitate that was partially soluble only in dmf. IR spectra of the latter solution indicate the presence of uncoordinated $[\text{Ni}_6(\text{CO})_{12}]^{2-}$. Because most of its salts are also well-soluble in less polar solvents, such as thf and acetone, the scarce solubility of the above material could be an indication of the formation of some Cd-rich copolymer containing intact $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ units, which is dismantled by dmf. ESI-MS spectra of dmf suspensions of this compound show the presence of $\{\text{CdCl}[\text{Ni}_6(\text{CO})_{12}]\}^-$ ($m/z = 836$) and $[\text{CdCl}_3]^-$ ($m/z = 219$) ions, which could result from the fragmentation of a $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]\}^\infty$ copolymer. The conclusion drawn from electrochemical studies of $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ (see next section) did not encourage further attempts to prepare $\{\text{Cd}_2\text{X}_3[\text{Ni}_6(\text{CO})_{12}]\}^\infty$ copolymers, as evidently the presence of Ni–Ni, Ni–Cd and chloride bridges (and perhaps, incipient Cd–Cd bonds) is not sufficient to guarantee electron communication between the $\text{Ni}_6(\text{CO})_{12}$ moieties and, therefore, should not enable relevant electron conduction along the intertriangular axis.

The reaction of $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ with $[\text{TBA}]\text{Cl}$ results in the formation of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ as outlined in Equation (5).



This is a further indication of the acid–base interaction existing in $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$, which is broken because of the attack of the Lewis base Cl^- at Cd^{II} .

Finally, $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ is nearly completely decomposed by a CO atmosphere into $\text{Ni}(\text{CO})_4$ and Cd^{II} salts. By carrying out the CO-induced decomposition of $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ in thf, the formation of very small amounts of a brown precipitate was noticed. This is soluble in acetonitrile and displays $\nu(\text{CO})$ at 1983(s) and 1798(m) cm^{-1} , fairly similar to those of the $[\text{Ni}_6(\text{CO})_{10}(\text{In}_2\text{Br}_5)_2]^{4-}$ species [$\nu(\text{CO})$ 1976(s) and 1784(m) cm^{-1}], which was previously obtained from the reaction of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ with InBr_3 .^[24] Its very meagre yields hampered further characterisation.

Aiming to extend the chemistry of bimetallic Ni–Cd carbonyl clusters, the reactions of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ with other Cd^{II} salts, such as CdF_2 , CdI_2 and $[\text{Cd}(\text{H}_2\text{O})_6][\text{BF}_4]_2$, were investigated. No reaction at all was observed with CdF_2 , whereas the other two reactions on the basis of IR monitoring completely parallel those with CdCl_2 . Thus, the final products can be formulated as $\{\text{Cd}_2\text{I}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ [$\nu(\text{CO})$ in thf at 2021(s), 1846(m) and 1822(m) cm^{-1}] and $\{\text{Cd}_2(\text{OH})_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ [$\nu(\text{CO})$ in thf at 2030(s), 1841(m) and 1819(m) cm^{-1}].

2.4. Electrochemical Studies

Figure 4 shows the redox activity of the trianion $[\text{Cd}_2\text{Cl}_3\{\text{Ni}_6(\text{CO})_{12}\}_2]^{3-}$ in thf solution.

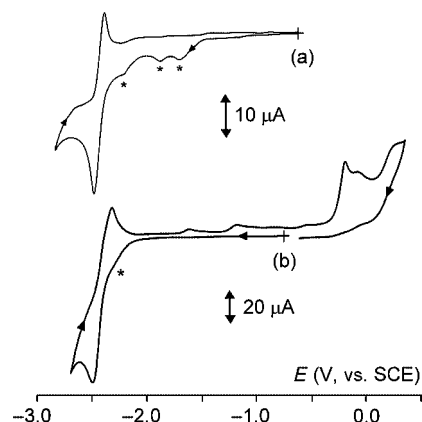


Figure 4. Cyclic voltammograms recorded at a gold electrode in thf solution of: (a) $[\text{NBu}_4]_3[\text{Cd}_2\text{Cl}_3\{\text{Ni}_6(\text{CO})_{12}\}_2]$ ($1.7 \times 10^{-3} \text{ mol dm}^{-3}$); (b) $[\text{NBu}_4]_2[\text{Ni}_6(\text{CO})_{12}]$ ($2.8 \times 10^{-3} \text{ mol dm}^{-3}$). $[\text{NBu}_4][\text{PF}_6]$ (0.2 mol dm^{-3}) supporting electrolyte. Scan rate 0.2 V s^{-1} .

Apart from a few unidentified processes (asterisked peaks) probably due to minor traces of impurities, the cyclic voltammogram exhibits one reduction, which displays features of partial chemical reversibility in the cyclic voltammetric timescale. In fact, analysis of the cyclic voltammetric responses with scan rates varying from 0.02 to 1.00 V s^{-1} showed that the current ratio $i_{\text{pa}}/i_{\text{pc}}$ is about 0.7 at the lowest scan rate and progressively increases up to about 0.9 at the highest scan rate. Concomitantly, the peak-to-peak separation tends to increase progressively from 64 to 180 mV , and the current function $i_{\text{pc}}\nu^{-1/2}$ decreases by about 10% for a 10 -fold increase in the scan rate. Such parameters are diagnostic for a (substantially) electrochemically reversible electron transfer coupled to slow chemical complications.^[25] Unfortunately, the very negative potential value of such a cathodic process ($E^\circ = -2.43 \text{ V}$, vs. SCE) prevented any reliable coulometric determination of the number of electrons involved.

To better define the nature of such a process, it seemed useful to look at the redox properties of the precursor dianion $[\text{Ni}_6(\text{CO})_{12}]^{2-}$. As illustrated in Figure 4b, the voltammogram exhibits two main irreversible oxidations ($E_{\text{pa}} = -0.22$ and $+0.25 \text{ V}$, respectively), and one reduction displaying features of chemical reversibility in the cyclic voltammetric timescale ($E^\circ = -2.41 \text{ V}$, vs. SCE), which is quite reminiscent of the cathodic process exhibited by $[\text{Cd}_2\text{Cl}_3\{\text{Ni}_6(\text{CO})_{12}\}_2]^{3-}$.

Cyclic voltammetric tests recorded in correspondence of the first anodic step at scan rates varying from 0.02 to 2.00 V s^{-1} showed that the process is rather complex, in that at high scan rates it splits into two separate processes, whereas the close-spaced minor peak ($E_{\text{pa}} = -0.08 \text{ V}$) tends to disappear. In addition, no directly associated response was detected in the backscan even at the highest scan rate.

Controlled potential coulometry ($E_w = 0.0 \text{ V}$) afforded a sudden decline in the electrolysis current after the consumption of about 0.6 – 0.7 electrons per molecule. Therefore, even if the process seems affected by electrode poisoning

effects probably caused by electrogenerated byproducts, it does not seem too ventured to assign it as a one-electron step. Interestingly, a cyclic voltammogram recorded on the solution resulting from the incomplete exhaustive oxidation showed a quite untouched cathodic pattern, thus indirectly supporting that, as reported above, the dimeric trianion $[\text{Cd}_2\text{Cl}_3\{\text{Ni}_6(\text{CO})_{12}\}_2]^{3-}$ arises from chemical oxidation of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$.

Also in this case, analysis of the cathodic cyclic voltammetric responses with scan rates varying from 0.02 to 1.00 V s^{-1} showed that: (1) the current ratio $i_{\text{pa}}/i_{\text{pc}}$ is about 0.7 at the lowest scan rate and progressively increases up to about 0.9 at the highest scan rate, (2) the peak-to-peak separation tends to increase progressively from 75 to 165 mV and (3) the current function $i_{\text{pc}}\nu^{-1/2}$ decreases by about 10% for a 10 -fold increase in the scan rate. In both cases, Osteryoung square-wave voltammetry did not appreciably improve the resolution of the voltammetric profiles.

On the basis of the above-mentioned coulometric measurements on the oxidation process of the monomeric dianion (which in cyclic voltammetry exhibits a peak-height substantially similar to that of the cathodic step), on the widths of the square wave peaks at half height (at 25° , $\Delta E_{\text{p}/2} = 126/n \text{ (mV)}$,^[25] which are 129 mV for $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ and 91 mV for $[\text{Cd}_2\text{Cl}_3\{\text{Ni}_6(\text{CO})_{12}\}_2]^{3-}$, and upon the fact that, under the same concentrations, the peak height of the dimer is about two times that of the monomer, we assign the reduction processes as a one-electron step in the case of the monomeric dianion and as a two-electron step in the case of the dimeric trianion. On this basis, it seems plausible to deduce that the two $[\text{Ni}_6(\text{CO})_{12}]$ subunits in $[\text{Cd}_2\text{Cl}_3\{\text{Ni}_6(\text{CO})_{12}\}_2]^{3-}$ are electronically noninteracting.

3. Conclusions

The work reported in this paper confirms the Lewis base donor ability of the triangular faces of the clusters $[\text{M}_3\text{n}(\text{CO})_{6\text{n}}]^{2-}$ ($\text{M} = \text{Ni}, \text{Pt}$) and the possibility of exploiting it to obtain oligomers and polymers based on MCC.^[16] The use of soft Lewis acids is of paramount importance to address the reaction directly on the metal core of the MCC ligands. These reactions result in new direct heteronuclear $\text{M}-\text{M}'$ bonds that, together with ancillary bridging halides ligands $\text{M}'-\text{X}_n-\text{M}'$, cooperate at the formation of oligomers or polymers held together by $\text{M}-\text{M}'-\text{X}_n-\text{M}'-\text{M}$ bridges.

The formation of the $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ dimer indicates some important differences between the reactions of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ and $[\text{Pt}_6(\text{CO})_{12}]^{2-}$ with CdCl_2 . In both cases, the reactions first proceeds by oxidation of $[\text{M}_6(\text{CO})_{12}]^{2-}$ ($\text{M} = \text{Ni}, \text{Pt}$) to give $[\text{M}_9(\text{CO})_{12}]^{2-}$ followed by addition of the Lewis acid to the metal frame of the cluster and resulting in the formation of the adducts $[\text{M}_9(\text{CO})_{18}\text{Cd}_2\text{Cl}_4]^{2-}$. Nonetheless, when $\text{M} = \text{Pt}$, this adduct is stable and it self-assembles upon crystallisation into a $1\text{D } \{\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2\}^\infty$ polymer by the formation of chloride brid-

ges.^[16] Conversely, the nickel analogue loses very easily a $[\text{Ni}_3(\text{CO})_6\text{Cl}]^-$ unit and is transformed into the $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ dimer. Intrinsically weaker Ni–Ni bonds relative to the Pt–Pt bonds and increasing intraunit steric repulsion between the carbonyl groups upon dimerisation may account for the observed difference.

The different products isolated in the case of Ni and Pt, i.e. $\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}^{3-}$ and $\{[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}\}_\infty$, display two alternative bridging modes of the Cd^{II} chloride derivatives, i.e. $[\text{Cd}(\mu\text{-Cl})_3\text{Cd}]^+$ and $\text{Cd}(\text{Cl})(\mu\text{-Cl})_2\text{Cd}(\text{Cl})$, and suggest that CdCl_2 can be a versatile reagent used to assemble MCC.

The redox condensation of $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ with halides MX_n of transition metals (e.g. Fe, Co, Rh, Pd, Pt, Cu, Ag, Au) and main group elements (e.g. C, Ge, Sn, Sb, Bi) has been widely exploited to obtain bi- and heterometallic MCC.^[1,26] The formation of acid–base adducts, i.e. $[\text{Ni}_6(\text{CO})_6(\mu_3\text{-CO})_5(\mu_3\text{-InBr}_3)(\eta^2\text{-}\mu_6\text{-In}_2\text{Br}_5)]^{3-}$, $[\text{Ni}_{12}(\text{CO})_{12}(\mu\text{-CO})_{10}(\mu_6\text{-In})(\eta^2\text{-}\mu_6\text{-In}_2\text{Br}_4\text{OH})]^{4-}$ and $[\text{Ni}_6(\text{CO})_{11}(\text{In}_2\text{Br}_5)_2]^{4-}$,^[24] was previously observed only in the case of InX_3 . This can be explained by the fact that both Cd^{II} and In^{III} are electropositive elements quite difficult to reduce, which form very weak homometallic bonds and with a high affinity for halides.

Electrochemistry suggests that the two $[\text{Ni}_6(\text{CO})_{12}]$ subunits present in the dimer are electronically independent. Attempts will be made in the future to replace the bridging Cd_2Cl_3 fragment with proper units that might favour the electronic interactions between the two peripheral clusters.

Experimental Section

General: All reactions and sample manipulations were carried out by using standard Schlenk techniques under an atmosphere of nitrogen and in dried solvents. The $[\text{Ni}_6(\text{CO})_{12}]^{2-}$ and $[\text{Ni}_9(\text{CO})_{18}]^{2-}$ ^[17,18] salts were prepared according to the literature. Analysis of Ni and Cd were performed by atomic absorption with a Pye-Unicam instrument. Analyses of C, H and N were obtained with a ThermoQuest FlashEA 1112NC instrument. IR spectra were recorded with a Perkin–Elmer SpectrumOne interferometer in CaF_2 cells. ESI mass spectra were recorded with a Waters Micro-mass ZQ4000 instrument. Cyclic voltammetry was performed in a three-electrode cell containing a platinum working electrode surrounded by a platinum-spiral counter electrode, and an aqueous saturated calomel reference electrode (SCE) mounted with a Luggin capillary. A BAS 100W electrochemical analyser was used as the polarising unit. All the potential values are referred to the saturated calomel electrode (SCE). Under the present experimental conditions, the one-electron oxidation of ferrocene occurs at $E^\circ = +0.59$ V in thf solution. Controlled potential coulometry was performed in an H-shaped cell with anodic and cathodic compartments separated by a sintered-glass disk. The working macroelectrode was a platinum gauze; a mercury pool was used as the counter electrode. Structure drawings were performed with SCHAKAL99.^[27]

$[\text{NBu}_4]_3\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\}$: $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.82 g, 3.59 mmol) was added in portions to a solution of $[\text{NBu}_4]_2[\text{Ni}_6(\text{CO})_{12}]$ (2.01 g, 1.71 mmol) in thf (40 mL) with stirring. The mixture was left to react for 2 h, and the resulting dark red solution was evaporated

to dryness. The residue was washed with water (40 mL) and extracted into thf (30 mL). Precipitation by slow diffusion of *n*-hexane (50 mL) gave a red crystalline precipitate composed of crystals of $[\text{NBu}_4]_3\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\} \cdot \text{thf}$ (yield 1.32 g, 61.5% based on Ni). The salt is soluble in thf, acetone, acetonitrile, dmf and dmsol, sparingly soluble in alcohols and insoluble in nonpolar solvents. IR (thf, 293 K): $\tilde{\nu} = 2025$ (vs), 1844 (m), 1819(m) cm^{-1} . $\text{C}_{76}\text{H}_{116}\text{Cd}_2\text{Cl}_3\text{N}_3\text{Ni}_{12}\text{O}_{25}$ (2507.39): calcd. C 36.41, H 4.66, N 1.68, Ni 28.09, Cd 8.97; found C 36.28, H 4.82, N 1.56, Ni 27.95, Cd 9.02.

X-ray Crystallographic Study: Crystal data and collection details for $[\text{NBu}_4]_3\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\} \cdot \text{thf}$ are reported in Table 2. The diffraction experiments were carried out with a Bruker APEX II diffractometer equipped with a CCD detector using $\text{Mo-K}\alpha$ radiation. Data were corrected for Lorentz polarisation and absorption effects (empirical absorption correction SADABS).^[28] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 .^[29] Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters, unless otherwise stated. The $[\text{Ni}_3(\text{CO})_6]$ unit bonded to Cd is disordered over three equally populated positions related by symmetry; similarly, the bridging chloride atom is disordered over two symmetry-related positions. Finally, the thf molecule appears disordered around the $\bar{3}$ axis over six symmetry-related positions. Only the independent part of the disordered groups were refined by using the following occupancy factors: 0.33333 for $[\text{Ni}_3(\text{CO})_6]$, 0.5 for Cl(1) and 0.16667 for thf. The overall occupancy for each group is one, after applying the related symmetry operations. All the disordered atoms were refined isotropically, except the three Ni and the Cl atoms which were refined anisotropically. Restraints were applied to the C–O distances of the anion, the C–N and C–C dis-

Table 2. Crystal data and experimental details for $[\text{NBu}_4]_3\{\text{Cd}_2\text{Cl}_3[\text{Ni}_6(\text{CO})_{12}]_2\} \cdot \text{thf}$.

Formula	$\text{C}_{76}\text{H}_{116}\text{Cd}_2\text{Cl}_3\text{N}_3\text{Ni}_{12}\text{O}_{25}$
<i>F</i> _w	2507.39
<i>T</i> [K]	193(2)
λ [Å]	0.71073
Crystal system	rhombohedral
Space group	$R\bar{3}c$
<i>a</i> [Å]	20.3179(8)
<i>b</i> [Å]	20.3179(8)
<i>c</i> [Å]	42.532(3)
α [°]	90
β [°]	90
γ [°]	120
Cell volume [Å ³]	15205.5(15)
<i>Z</i>	6
<i>D</i> _{calcd.} [g cm ^{−3}]	1.643
μ [mm ^{−1}]	2.725
<i>F</i> (000)	7656
Crystal size [mm]	0.22 × 0.16 × 0.13
θ limits [°]	1.50–25.03
Index ranges	−24 ≤ <i>h</i> ≤ 24 −24 ≤ <i>k</i> ≤ 24 −50 ≤ <i>l</i> ≤ 50
Reflections collected	46319
Independent reflections	2994 [<i>R</i> _{int} = 0.0340]
Completeness to $\theta = 25.03^\circ$	100%
Data/restraints/parameters	2994/79/230
Goodness on fit on F^2	1.026
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0551
<i>wR</i> ₂ (all data)	0.1765
Largest diff. peak and hole [e Å ^{−3}]	0.669/−0.786

tances of the NBu_4^+ cation and to the C–O and C–C distances of the thf molecule to obtain a satisfactory model.

CCDC-633786 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- [1] C. Femoni, M. C. Iapalucci, F. Kaswalder, G. Longoni, S. Zacchini, *Coord. Chem. Rev.* **2006**, 250, 1580–1604.
- [2] J. C. Calabrese, L. F. Dahl, P. Chini, G. Longoni, S. Martinengo, *J. Am. Chem. Soc.* **1974**, 96, 2614–2616; G. Longoni, P. Chini, *J. Am. Chem. Soc.* **1976**, 98, 7225–7231.
- [3] C. Femoni, M. C. Iapalucci, G. Longoni, P. H. Svensson, *Chem. Commun.* **2004**, 2274–2275.
- [4] C. Femoni, M. C. Iapalucci, G. Longoni, P. Svensson, J. Wolowska, *Angew. Chem. Int. Ed.* **2000**, 39, 1635–1637.
- [5] N. T. Tran, M. Kawano, D. R. Powell, L. F. Dahl, *J. Am. Chem. Soc.* **1998**, 120, 10986–10987.
- [6] N. T. Tran, L. F. Dahl, *Angew. Chem. Int. Ed.* **2003**, 42, 3533–3537.
- [7] N. T. Tran, D. R. Powell, L. F. Dahl, *Angew. Chem. Int. Ed.* **2000**, 39, 4121–4125.
- [8] L. H. Gade, B. F. G. Johnson, J. Lewis, M. McPartlin, H. R. Powell, *J. Chem. Soc. Chem. Commun.* **1990**, 110–111.
- [9] M. A. Beswick, J. Lewis, P. R. Raithby, M. C. Ramirez de Arellano, *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 291–293.
- [10] M. A. Beswick, J. Lewis, P. R. Raithby, M. C. Ramirez de Arellano, *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 2227–2228.
- [11] D. S. Shephard, T. Maschmeyer, B. F. G. Johnson, J. M. Thomas, G. Sankar, D. Ozkaya, W. Zhou, R. D. Oldroyd, R. G. Bell, *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 2242–2245.
- [12] B. T. Heaton, L. Strona, S. Martinengo, D. Strumolo, V. G. Albano, D. Braga, *J. Chem. Soc. Dalton Trans.* **1983**, 2175–2182.
- [13] T. Nakajima, A. Ishiguro, Y. Wakatsuki, *Angew. Chem. Int. Ed.* **2001**, 40, 1066–1068.
- [14] C. E. Plechnik, S. Liu, X. Chen, E. A. Meyers, S. G. Shore, *J. Am. Chem. Soc.* **2004**, 126, 204–213.
- [15] a) C. Femoni, F. Kaswalder, M. C. Iapalucci, G. Longoni, M. Mehlstäubl, S. Zacchini, A. Ceriotti, *Angew. Chem. Int. Ed.* **2006**, 45, 2060–2062; b) C. Femoni, F. Kaswalder, M. C. Iapalucci, G. Longoni, S. Zacchini, *Eur. J. Inorg. Chem.* **2007**, 1483–1486.
- [16] C. Femoni, F. Kaswalder, M. C. Iapalucci, G. Longoni, S. Zacchini, *Chem. Commun.* **2006**, 2135–2137.
- [17] a) J. C. Calabrese, L. F. Dahl, A. Cavalieri, P. Chini, G. Longoni, S. Martinengo, *J. Am. Chem. Soc.* **1974**, 96, 2616–2618; b) G. Longoni, P. Chini, A. Cavalieri, *Inorg. Chem.* **1976**, 15, 3025–3027.
- [18] a) G. Longoni, P. Chini, L. D. Lower, L. F. Dahl, *J. Am. Chem. Soc.* **1975**, 97, 5034–5036; b) G. Longoni, P. Chini, *Inorg. Chem.* **1976**, 15, 3029–3031.
- [19] D. Braga, F. Grepioni, P. Milne, E. Parisini, *J. Am. Chem. Soc.* **1993**, 115, 5115–5122.
- [20] A. Ceriotti, P. Chini, R. Della Pergola, G. Longoni, *Inorg. Chem.* **1983**, 22, 1595–1598.
- [21] S. N. Titova, V. T. Bychkov, G. A. Domrechev, G. A. Razuvaev, M. T. Strachkov, L. N. Zacharov, *J. Organomet. Chem.* **1980**, 187, 167–174.
- [22] a) A. Washowska, T. Lis, U. Krewska, Z. Czaplá, *Acta Crystallogr., Sect. C* **1990**, 46, 1768–1770; b) U. Walther, D. Brinkmann, G. Chapuis, H. Arend, *Solid State Commun.* **1978**, 27, 901–905; c) S. Kashida, S. Sato, *J. Phys. Soc. Jpn.* **1985**, 54, 2934–2939; d) A. B. Corradi, M. R. Cramarossa, M. Saladini, *Inorg. Chim. Acta* **1997**, 257, 19–26; e) A. B. Corradi, M. R. Cramarossa, M. Saladini, L. B. Battaglia, J. Giusti, *Inorg. Chim. Acta* **1995**, 230, 59–65; f) S. Kashida, Y. Ito, S. Sato, *J. Solid State Chem.* **1987**, 69, 258–266.
- [23] a) Z. Zhu, R. C. Fischer, J. C. Fetting, E. Rivard, M. Brynda, P. P. Power, *J. Am. Chem. Soc.* **2006**, 128, 15068–15069; b) R. Faggiani, R. J. Gillespie, J. E. Vekris, *J. Chem. Soc. Chem. Commun.* **1986**, 517–518.
- [24] F. Demartin, M. C. Iapalucci, G. Longoni, *Inorg. Chem.* **1993**, 32, 5536–5543.
- [25] P. Zanello in *Inorganic Electrochemistry: Theory, Practice and Application*, RSC, Cambridge, UK, **2003**.
- [26] P. D. Mlynek, M. Kawano, M. A. Kozee, L. F. Dahl, *J. Cluster Sci.* **2001**, 12, 313–338.
- [27] E. Keller, *SCHAKAL99*, University of Freiburg, Germany, **1999**.
- [28] G. M. Sheldrick, *SADABS: Program for Empirical Absorption Correction*, University of Göttingen, Germany, **1996**.
- [29] G. M. Sheldrick, *SHELX97: Program for Crystal Structure Determination*, University of Göttingen, Germany, **1997**.

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