

Redox Behavior of $[H_{6-n}Ni_{38}Pt_6(CO)_{48}]^{n-}$ ($n = 4-6$) Anions: A Series of Metal Carbonyl Clusters Displaying Electron-Sink Features

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An investigation of the chemical and electrochemical redox behavior of the bimetallic $[H_{6-n}Ni_{38}Pt_6(CO)_{48}]^{n-}$ ($n = 4-6$) clusters shows that they display electron-sink features encompassing up to six different oxidation states. As a corollary, these studies provide an indirect proof of the presence of hydride atoms where $n = 4$ and 5. The difference in the formal electrode potentials of consecutive redox couples of both $[HNi_{38}Pt_6(CO)_{48}]^{5-}$ and $[Ni_{38}Pt_6(CO)_{48}]^{6-}$ is almost constant and amounts on the average to ca. 0.33 and 0.28 V, respectively. Such constancy of ΔE within each species points out the absence of a well-defined HOMO–LUMO gap in both clusters. Besides, its value is an indication of their semiconductor rather than metallic nature. A plot of the average ΔE exhibited by the known carbonyl clusters displaying electrochemically reversible multiple redox changes versus their nuclearity suggests that the transition from semiconductor to metallic behavior might occur upon a ca. 50% increase of the today available cluster nuclearities.

Introduction

Because of the work of L. F. Dahl¹ and complementary work carried out in our laboratory,² a wide series of icosahedral nickel carbonyl clusters containing group 14–16 elements has been synthesized. This comprises non-centered $[Ni_{10}(\mu_5-ER)_2(CO)_{18}]^{2-}$ ($E = P, As, Sb, Bi; R = \text{alkyl or aryl substituent}$),^{1a-e} E-centered $[Ni_{12}(\mu_{12}-E)(CO)_{22}]^{2-}$,^{2a} Ni-centered $[Ni_{10}(\mu_{12}-Ni)(\mu_6-E)_2(CO)_{18}]^{n-}$ ($E = Sb, Bi, Se$),^{1f,2d,e} and $[Ni_{10}(\mu_{12}-Ni)(\mu_6-ER)_2(CO)_{18}]^{n-}$ ($E = Sn, R = \text{alkyl substituent}; ^1g E = Sb, R = Ni(CO)_3$).^{2b,c} The non-centered and E-centered nickel clusters possess the expected number of skeletal electron pairs (SEP) and do not display any reversible redox propensity. In contrast, the Ni-centered species

show a higher number of SEP and electrochemically reversible redox aptitudes. In particular, the Ni-centered $[Ni_{10}(\mu_{12}-Ni)(\mu_6-E)_2(CO)_{18}]^{n-}$ ($E = Sb, Bi$) and $[Ni_{10}(\mu_{12}-Ni)(\mu_6-Sb \rightarrow Ni(CO)_3)_2(CO)_{18}]^{n-}$ derivatives display three different oxidation states, which are sufficiently long-lived to permit isolation of each species. Homoleptic carbonylmetal clusters rarely display a redox propensity^{3,4} comparable to that shown, for instance, by the Fe–S cubane clusters⁵ or fullerenes.⁶ EHMO analysis of several $Ni_{10}(\mu_{12}-M)E_2(CO)_{18}$ model compounds pointed out that the out-of-phase combinations of the d orbitals of the interstitial atom with those of the icosahedral $Ni_{10}E_2$ cage were sufficiently low in energy to be populated by electrons when $M = Ni$.^{2(c)} This justified the exceptional electron count of the Ni-centered clusters. Furthermore, it suggested that the presence of an interstitial nickel atom and concomitant stabilization of the metal core imparted by the peripheral main-group elements could trigger electron-sink behavior also in carbonyl clusters. This conclusion was later authorized by electrochemical studies of $[Ni_{32}(\mu_8-C)_6(CO)_{36}]^{6-}$ and $[H_{6-n}Ni_{38}(\mu_8-C)_6(CO)_{42}]^{n-}$ ($n = 4-6$), which contain highly connected (12 and 13) nickel and bulk carbide atoms.⁷ Indeed, these high-nuclearity carbide

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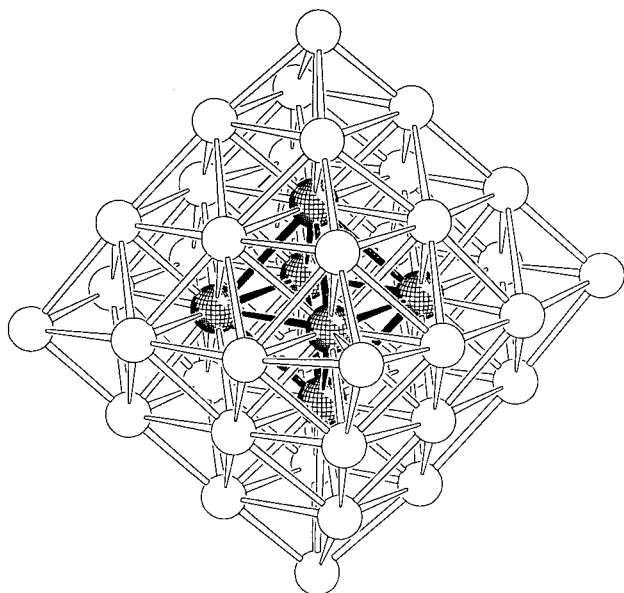


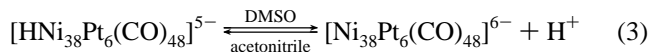
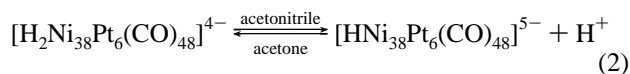
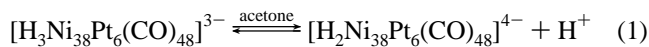
Figure 1. The metal frame of the $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$ penta-anion.

clusters display a wide redox aptitude encompassing five redox changes with features of electrochemical reversibility.^{7c}

The clusters containing interstitial platinum atoms apparently show contrasting cyclic voltammetric behavior. Both $[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$ and $[\text{Pt}_{24}(\text{CO})_{30}]^{2-}$ exhibit electrochemically reversible redox changes.^{4a,8a,b} In contrast, $[\text{Pt}_{26}(\text{CO})_{32}]^{2-}$ and $[\text{Pt}_{38}(\text{CO})_{44}]^{2-}$ display mainly irreversible behavior.^{8b} It was, therefore, of interest to investigate the related chemical and electrochemical redox behavior of bimetallic $[\text{H}_{6-n}\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{n-}$ ($n = 4-6$) clusters, which contain six interstitial platinum atoms.⁹ These have been found to display electron-sink features comparable to those of the $[\text{Ni}_{32}(\mu_8\text{-C})_6(\text{CO})_{36}]^{6-}$ and $[\text{H}_{6-n}\text{Ni}_{38}(\mu_8\text{-C})_6(\text{CO})_{42}]^{n-}$ ($n = 4-6$) clusters. As a corollary, these studies provide an indirect proof of the presence of hydride atoms when $n = 4$ and 5 .

Results and Discussion

The synthesis and the complete structural characterization of the $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$ penta-anion have been reported.^{9a} Its "cherry" $\text{Ni}_{38}\text{Pt}_6$ metal frame is depicted in Figure 1. Other structural investigations carried out on crystals of the corresponding tetra- and hexa-anions disclosed the presence of an identical metal frame. However, their full structure could not be determined owing to the poor quality of their crystals.^{9a,b} The $[\text{H}_{6-n}\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{n-}$ ($n = 3-5$) members of the above series were formulated as hydrides on the basis of their progressive *deprotonation equilibria* in solvents of increasing dielectric constant (eqs 1–3).⁹ Unfortunately, NMR experiments could not substantiate the presence of hydride atoms.



The above purported deprotonation equilibria eqs (1–3) and the low molar solubility of the tetrasubstituted ammonium or phosphonium salts of $[\text{H}_{6-n}\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{n-}$ ($n = 4-6$) in all organic solvents strongly limited the choice of the solvent for redox studies. Concentrations of the $[\text{H}_{6-n}\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{n-}$ ($n = 4-6$) salts suitable for electrochemical studies could only be obtained in dimethylformamide (DMF) and acetonitrile solutions. Nevertheless, the observed current densities were very low due to the conceivably low diffusion coefficients. The $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$ hydride is unaffected by these solvents. On the contrary, $[\text{H}_2\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{4-}$ significantly deprotonates to the former, as inferred from IR monitoring of the solutions, according to eq 2.

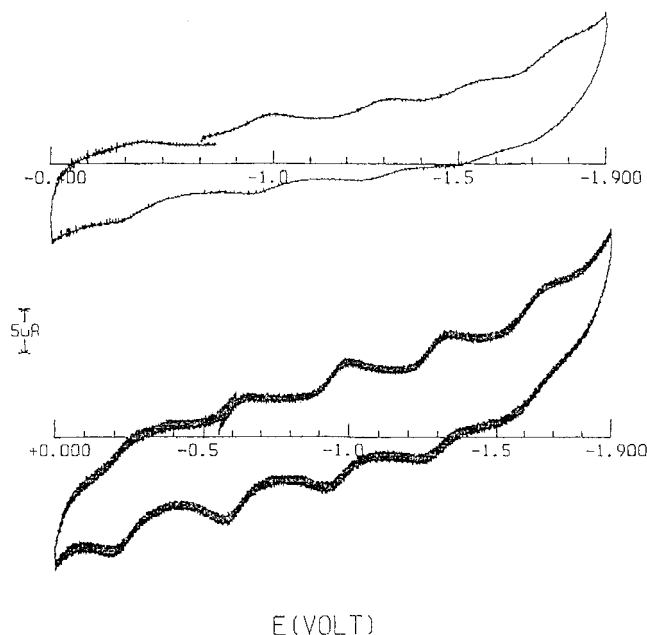


Figure 2. Cyclic voltammograms of (a) $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{6-}$ (4×10^{-4} M) and (b) $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$ (4×10^{-4} M) recorded at a platinum electrode. DMF solution containing $[\text{NBu}_4][\text{PF}_6]$ (0.2 M). Scan rate 0.2 V s^{-1} .

Nevertheless, the observed current densities were very low due to the conceivably low diffusion coefficients. The $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$ hydride is unaffected by these solvents. On the contrary, $[\text{H}_2\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{4-}$ significantly deprotonates to the former, as inferred from IR monitoring of the solutions, according to eq 2.

We found that $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{6-}$ and $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$ display an unusually rich redox aptitude and exhibit five redox processes having features of chemical and electrochemical reversibility on the cyclic voltammetric time scale. Typical cyclic voltammograms are shown in Figure 2. The low current density made rather troublesome the experimental measurement of the number of electrons involved in each redox step by controlled potential coulometry. At any rate, the first two reduction steps were one-electron processes for both $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{6-}$ and $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$. Because of the presence of multiple redox steps of equal intensity, we may confidently assume that also the remaining redox changes of both species are mono-electronic. The formal electrode potentials of the electron transfers displayed by $[\text{H}_{6-n}\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{n-}$ ($n = 5, 6$) are summarized in Table 1. In all cases, attribution of the occurring redox change has been made by voltammetry at mercury or platinum electrodes with periodical renewal of the diffusion layer.¹⁰ This proves that $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{6-}$ undergoes one oxidation and four reductions, whereas $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$ undergoes one or two oxidations (depending on the working electrode) and three reductions.

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Table 1. Formal Electrode Potentials (in V, vs SCE) for the Redox Changes Exhibited by the $[\text{H}_{6-n}\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{n-}$ ($n = 5, 6$) Clusters in DMF and Acetonitrile Solution

compound	$E^{\circ'}_{3^{-}/4^{-}}$	$E^{\circ'}_{4^{-}/5^{-}}$	$E^{\circ'}_{5^{-}/6^{-}}$	$E^{\circ'}_{6^{-}/7^{-}}$	$E^{\circ'}_{7^{-}/8^{-}}$	$E^{\circ'}_{8^{-}/9^{-}}$	$E^{\circ'}_{9^{-}/10^{-}}$
$[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{6-}$ ^{a,b}			-0.62	-0.97	-1.29	-1.54	-1.75
$[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$ ^{a,b}		-0.61	-0.98	-1.28	-1.55		
$[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$ ^{c,b}	-0.25	-0.62	-0.96	-1.28	-1.62		
$[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$ ^{c,d}	-0.28	-0.60	-0.93	-1.25	-1.58		

^a Measured by using an Hg electrode. ^b DMF as solvent. ^c Measured by using a Pt electrode. ^d Acetonitrile as solvent.

The $[\text{H}_2\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{4-}$ tetraanion also exhibits redox aptitude; however, its partial deprotonation in acetonitrile to $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$ (see eq 2), combined with a low current density, gives rise to overlapped and broad cyclic voltammetric profiles. Owing to that, the redox potentials were barely reproducible. Therefore, this species has not been investigated in more details.

The above experiments indirectly support the chemical evidences of the hydride nature of $[\text{H}_{6-n}\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{n-}$ ($n = 4, 5$). Thus, the differences in the voltammetric responses in the three cases can only be interpreted as due to the perturbing effect of the presence of hydride atoms. Furthermore, the electrochemical experiments on $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{6-}$ point out the reversible access only to the corresponding pentaanion, whereas the sequential formation of isoelectronic penta-, tetra-, and trianion is obtained upon protonation.⁹ The possible existence of a given anion both as even-electron hydride and odd-electron paramagnetic species has previously been documented in lower nuclearity clusters, e.g., the $[\text{HFe}_5(\mu_3\text{-S})_2(\text{CO})_{14}]^-/[\text{Fe}_5(\mu_3\text{-S})_2(\text{CO})_{14}]^-$ pair of compounds.¹¹

Interestingly, the redox potentials of the first oxidation of $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{6-}$ and the first oxidation of $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$ are very close in value; the same holds for the other redox processes. It should be noted, however, that at the potential of the redox couple $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{6-}/5^-$ the deprotonated pentaanion undergoes a reduction step, whereas the protonated $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$ undergoes an oxidation step. This behavior is understandable in terms of electron occupancy. Thus, the 5-/6- change of $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{6-}$ corresponds to the 4-/5- change of $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$ being the two species isoelectronic. A related diagonal correspondence holds for the other redox changes. A similar behavior has previously been observed in the $[\text{H}_{6-n}\text{Ni}_{38}(\mu_8\text{-C})_6(\text{CO})_{42}]^{n-}$ ($n = 5, 6$) series,^{7c} but not for the $[\text{Ru}_{10}(\mu_6\text{-C})(\text{CO})_{24}]^{2-}$ and $[\text{HRu}_{10}(\mu_6\text{-C})(\text{CO})_{24}]^-$ pairs of clusters.¹² In the latter case, the irreversible reduction of the dianion occurs at a more negative potential than the corresponding irreversible reduction of the isoelectronic hydride monoanion. If allowance is made to neglect the non-thermodynamic meaning of irreversible processes, such a difference could arise from a different stereochemistry of the hydride atom (e.g., interstitial rather than edge bridging, as in the latter). Indeed interstitial atoms do not alter the number of bonding orbitals of a given cluster because the interaction of their orbitals with those of the cage generates an equal number of bonding and antibonding orbitals.¹³ Therefore, it seems reasonable to suggest that a hydride atom interstitially lodged in one of the miscellaneous octahedral cavities of $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$ would have little influence on the energy and composition of its frontier orbitals.

The second main difference between the electrochemical responses of $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$ and $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{6-}$ is

Table 2. Infrared Carbonyl Absorptions of the $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{n-}$ ($n = 5-9$) Anions

compound	solvent	$\nu_{\text{CO}}(\pm 2 \text{ cm}^{-1})$
$[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$	CH_3CN	2003 s, 1861 ms
$[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$	CH_3CN	2005 s, 1862 ms
$[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$	DMF	2003 s, 1860 ms
$[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{6-}$	DMF	1990 s, 1845 ms
$[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{7-}$	DMF	1980 s, 1830 ms
$[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{8-}$	DMF	1968 s, 1820 ms
$[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{9-}$	DMF	1956 s, 1802 ms

constituted by the presence of an extra oxidation process at -0.25 V in the former and an extra reduction process at -1.75 V in the latter. Apparently, that represents the only perturbing effect of neutralizing one of the negative charges of the hexaanion with a proton.

The electrochemical results have partially been validated by chemical reduction of $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{6-}$ with sodium naphthalene in DMF by monitoring with IR. The stepwise addition of three equivalents of reducing agent gives rise to a decrease of $10-15 \text{ cm}^{-1}$ per equivalent in the frequency of the infrared carbonyl absorptions (see Table 2). This can be considered as an evidence of the sequential formation of the hepta-, octa-, and nona-anion. Indeed, such shift is in the opposite direction and close in value to that observed upon sequential protonation of $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{6-}$.⁹ The observed species are stable in solution under a rigorously inert atmosphere, as inferred from their IR features after several hours. However, their attempted isolation in the solid-state failed owing to partial reoxidation during the workout. The sequential addition of 3 equiv of tropylium tetrafluoroborate to $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{9-}$ quantitatively regenerates the parent $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{6-}$ hexaanion, through the intermediate formation of $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{8-}/7^-$. Addition of 1 equiv of the oxidizing agent to $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{6-}$, both in DMF and acetonitrile, leads to a species which shows infrared carbonyl absorptions coincident with those of $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$. Whether this is the even-electron $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$ or the odd-electron $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$ could not be unambiguously established owing to lack of both EPR and NMR response of its solution. However, the stability of this species in a highly ionizing solvent such as DMSO strongly favors the second hypothesis.

The reported electrochemical results point out the existence of two different series of clusters having the following general formulas: $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{n-}$ ($n = 5-10$) and $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{n-}$ ($n = 3-8$). Despite a widespread belief that clusters are electron reservoirs,^{3,5} a redox aptitude such as that of $[\text{H}_{6-n}\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{n-}$ ($n = 5, 6$) is rather exceptional for homoleptic carbonylmetal clusters.^{3,4} Other relevant examples are $[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$ ^{4a} and $[\text{Pt}_{24}(\text{CO})_{30}]^{2-}$,⁸ both containing interstitial platinum atoms. These undergo consecutive pairs of close-spaced one-electron redox changes with features of electrochemical reversibility, separated by ca. $0.5-0.7$ V. It seems, therefore, reasonable to conclude that the presence of bulk

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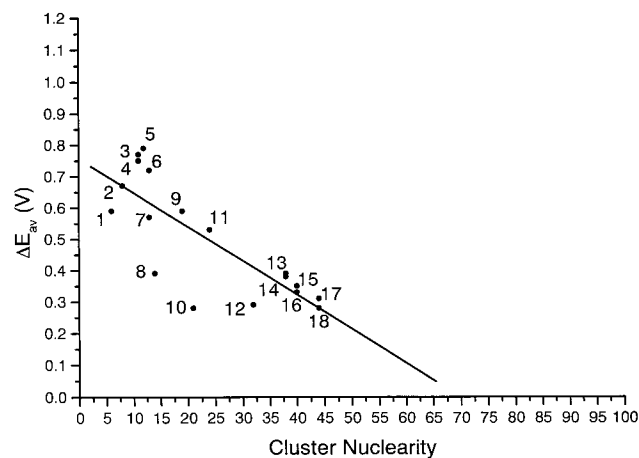


Figure 3. A linear plot of the experimental average separation between the formal electrode potentials of consecutive redox couples (ΔE_{av} in V) as a function of nuclearity of the cluster: 1, $[\text{Fe}_3\text{Pt}_3(\text{CO})_{15}]^{n-}$ ($n = 0-2$);¹⁴ 2, $[\text{Co}_8\text{C}(\text{CO})_{18}]^{n-}$ ($n = 1-4$);^{4a} 3, $[\text{Ni}_{11}\text{Sb}_2(\text{CO})_{18}]^{n-}$ ($n = 2-4$);^{2c} 4, $[\text{Ni}_{11}\text{Bi}_2(\text{CO})_{18}]^{n-}$ ($n = 2-4$);^{2d} 5, $[\text{HFe}_6\text{Pd}_6(\text{CO})_{24}]^{n-}$ ($n = 2-5$);¹⁶ 6, $[\text{Ni}_{13}\text{Sb}_2(\text{CO})_{24}]^{n-}$ ($n = 2-4$);^{2c} 7, $[\text{Co}_{13}\text{C}_2(\text{CO})_{24}]^{n-}$ ($n = 3-6$);^{4a} 8, $[\text{Ir}_{14}(\text{CO})_{27}]^{n-}$ ($n = 0-2$);¹⁷ 9, $[\text{Pt}_{19}(\text{CO})_{22}]^{n-}$ ($n = 3-7$);^{4a} 10, $[\text{Ag}_{13}\text{Fe}_8(\text{CO})_{32}]^{n-}$ ($n = 3-5$);¹⁸ 11, $[\text{Pt}_{24}(\text{CO})_{30}]^{n-}$ ($n = 1-5$);⁸ 12, $[\text{Ni}_{32}\text{C}_6(\text{CO})_{36}]^{n-}$ ($n = 5-10$);^{7c} 13, $[\text{HNi}_{38}\text{C}_6(\text{CO})_{42}]^{n-}$ ($n = 4-8$);^{7c} 14, $[\text{Ni}_{38}\text{C}_6(\text{CO})_{42}]^{n-}$ ($n = 5-9$);^{7c} 15, $[\text{HNi}_{36}\text{Pt}_4(\text{CO})_{45}]^{n-}$ ($n = 4-7$);^{15b} 16, $[\text{Ni}_{36}\text{Pt}_4(\text{CO})_{45}]^{n-}$ ($n = 5-9$);^{15b} 17, $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{n-}$ ($n = 3-7$); 18, $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{n-}$ ($n = 5-9$).

platinum, as well as nickel, can trigger electron-sink behavior also in homoleptic carbonylmetal clusters.

The present results and the data available in the literature^{3,4} suggest that the average separations between the formal electrode potentials of consecutive redox couples of carbonyl clusters displaying multiple reversible redox changes decrease as a function of the nuclearity. Indeed, the consecutive one-electron transitions progressively become almost equally spaced (on the average 0.28 and 0.33 V for $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{6-}$ and $[\text{HNi}_{38}\text{Pt}_6(\text{CO})_{48}]^{5-}$, respectively) and closer. A collection of average ΔE plotted versus nuclearity is shown in Figure 3. Assumption of a linear dependence suggests that upon a ca. 50% increase of the nuclearity of the cluster the ΔE_{av} will reach a value beyond which disproportionation equilibria could become significant. It should be noted that the correlation coefficient of the fit of Figure 3 is rather poor because of the wide dispersion of the ΔE_{av} for a given nuclearity. This arises from the fact that all homoleptic carbonyl clusters displaying multiple redox changes have been included in Figure 3, regardless of their composition and stereogeometry. Besides, some entries represent the average value of a set of rather dispersed consecutive ΔE values. Segregated data of clusters containing bulk nickel or platinum atoms, for instance, give very satisfactory linear correlation coefficients up to 99.6% level. However, these plots are less general and the fit is less significant because of the present paucity of data.

A further implication stems from fact that the separations between the formal electrode potentials of consecutive redox couples (ΔE values) of the above clusters should mainly mirror the differences between their ionization energies. These, in their turn, may be extrapolated to quantify the energy separation

between the frontier one-electron energy levels. Within this premise, the almost constant spacing found in $[\text{H}_{6-n}\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{n-}$ ($n = 5, 6$) first points out the absence of a well-defined HOMO–LUMO gap, as it has been anticipated by theoretical calculations on a model $[\text{Ni}_{44}(\text{CO})_{48}]^{n-}$ compound.¹⁹ Second, it allows to gather an approximate value of 0.3 eV for the average energy separation between the frontier one-electron energy levels of $[\text{H}_{6-n}\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{n-}$ ($n = 5, 6$). Such an energy separation suggests that these clusters should still have semiconductor rather than metallic nature. However, according to Figure 3, the transition from semiconductor to metallic behavior might occur for clusters with a nuclearity beyond a value of ca. 65. As above, this threshold should only be taken as a crude attempt to experimentally envision where transition from semiconductor to metallic behavior of a homoleptic carbonyl cluster might be expected to occur. It is worth of note that such a nuclearity is not beyond reach, as shown by the recent isolation of the carbonyl-substituted $\text{Pd}_{59}(\text{CO})_{32}(\text{PMe}_3)_{21}$ derivative,²⁰ that represents the highest nuclearity cluster so far fully characterized by X-ray studies. Furthermore, it seems rewarding that spectroscopic studies on CO adsorbed on palladium islands deposited on alumina film point out that aggregation of ca. 100 Pd atoms is necessary in order to observe transition from molecular to metallic features.²¹

Experimental Section

Apparatus and materials for electrochemical measurements are described elsewhere.²² Potential values are referred to the saturated calomel electrode (SCE). Under the present experimental conditions the one-electron oxidation of ferrocene occurs at $E^{\circ} = +0.38$ V in acetonitrile and +0.47 V in DMF. The $[\text{H}_{6-n}\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}]^{n-}$ ($n = 4-6$) anions have been prepared according to literature,^{9,15} isolated as NMe_4^+ salts, and crystallized from acetonitrile and diisopropyl ether.

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