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# Theoretical analysis of the Mackay icosahedral cluster $\mathrm{Pd}_{55}\left(\mathrm{P}^{\mathrm{i}} \mathrm{Pr}_{3}\right)_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}$ : An open-shell 20 -electron superatom* 

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*Dedicated to Professor D. Mike P. Mingos on the occasion of his 75th birthday.


#### Abstract

The electronic structure of the spherical Mackay icosahedral nanosized cluster $\mathrm{Pd}_{55}\left(\mathrm{P}^{\prime} \mathrm{Pr}_{3}\right)_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}$ is analyzed using DFT calculations. Results reveal that it can be considered as a regular superatom with a "magic" electron count of 20 , characterized by a $1 S^{2}$ $1 P^{6} 1 D^{10} 2 S^{2}$ jellium configuration. Its open shell nature is associated with partial occupation of non-jellium, $4 d$-type, levels located on the interior of the $\mathrm{Pd}_{55}$ kernel. This shows that the superatom model can be used to rationalise the bonding and stability of spherical ligated group-10, clusters, despite their apparent 0-electron count.


## Introduction

In 2016, the first isolation of the crystalline icosahedral Mackay $\mathrm{Pd}_{55}\left(\mathrm{PiPr}_{3}\right)_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}(1)$ cluster was reported. ${ }^{[1]}$ This fascinating compound that ideally conforms to $I_{h}$ symmetry (without isopropyl substituents) is somewhat unique. The Matryoshka doll-like 55-metal-atom two-shell cluster architecture consists of a centered $\mathrm{Pd}_{13}$ icosahedron encapsulated within a $\mathrm{Pd}_{42}$ icosahedron. In $I_{h}$ symmetry, the outer icosahedron is made of two different types of symmetry equivalent vertices, of 12 and 30 degeneracy respectively. The whole ${\mathrm{Pd} @ \mathrm{Pd}_{12} @ \mathrm{Pd}_{42} \text { metal kernel }}^{2}$ corresponds to a so-called MacKay "hard-sphere" model. ${ }^{[2]}$ Mackay icosahedra are densely packed assemblies of equalsized spheres which are characterized by specific numbers of spheres (atoms), 13, 55, 147, 309, etc. forming concentric shells, $1,2,3,4$, etc., respectively. ${ }^{[2]}$ The $\mathrm{Pd}_{55}$ kernel of 1 is the first crystallographically documented molecular example of a Mackay icosahedron. ${ }^{[1]}$ The 12 outer Pd atoms that are located on the $C_{5}$ axis are coordinated by a phosphine ligand, whereas 20 symmetry-equivalent triangular faces of the $\mathrm{Pd}_{42}$ outer shell (metal atoms not attached to the 12 phosphine ligands) are
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capped by carbonyl ligands. The icosahedral two-shell Pd architecture of $\mathrm{Pd}_{55}\left(\mathrm{PiPr}_{3}\right)_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}$ is shown in Figure 1.

(a)

Figure 1. Structural arrangement of $\mathrm{Pd}_{55}\left(\mathrm{Pi}^{\prime} \mathrm{Pr}_{3}\right)_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}$ : a) "Matryoshka doll
 surrounding ligands (isopropyl groups not shown for clarity). The purple, yellow, dark blue, orange, grey, and red spheres are central Pd (Pd'), inner Pd (Pd"), outer $\mathrm{Pd}\left(\mathrm{Pd}^{\prime \prime \prime}\right), \mathrm{P}, \mathrm{C}$, and O atoms, respectively. ${ }^{[1]}$

The structure and bonding properties of stable (viable ${ }^{[3]}$ ) inorganic clusters, are usually governed by their numbers of valence electrons. Indeed, as for any stable molecular compound, there are strong relationships between the structure and the electron count of clusters. Such relationships are based on the closedshell principle and assume that no antibonding orbital is occupied. In the case of organometallic transition-metal clusters, these relationships are issued from the polyhedral skeletal electron pair (PSEP) theory, ${ }^{[4]}$ of which the Wade-Mingos electron-counting rules ${ }^{[5-9]}$ are the most popularized. These rules generally apply well to hollow clusters made of metal atoms, the valence $d$ orbitals of which participate to the bonding. This is not the case for group 11 metal clusters, for example, which have their (localized) valence $d$ shell filled and then can be ignored in the count of bonding electrons. ${ }^{[10]}$ Thus, group 11 metals participate to the bonding mainly with their valence s orbitals. They usually tend to aggregate in a compact (non-hollow) and often spherical way. To understand their structure and composition, the concept of superatom, ${ }^{[8-24]}$ based on the spherical jellium model, ${ }^{[25-27]}$ is used. This qualitative model considers electrons within a radial phenomenological potential supposed to describe the average electrostatic potential associated with the cluster atom nuclei.

Thus, the spherical jellium model does not consider explicitly the atom nuclei. On the other side, it allows describing the cluster electronic structure in terms of superatomic orbitals, somewhat similar to atomic orbitals, but extending over the whole cluster sphere. Their shell ordering is largely independent from the cluster composition and spans as $1 \mathrm{~S}<1 \mathrm{P}<1 \mathrm{D}<2 \mathrm{~S}<1 \mathrm{~F}$, etc. As for atomic systems, closed-shell (noble gas) stability will be achieved for specific ("magic") electron counts, i.e., 2, 8, 18, 20, 34 , etc. It is of note that the superatom approach considers only the delocalized electrons that are responsible for the bonding within the cluster kernel. In a regular LCAO-MO DFT calculations on group 11 clusters, these electrons are identified as those occupying the Kohn-Sham orbitals of dominant valence $s$ character. ${ }^{[10,14-18,20]}$ It turns out that most of the coinage metal clusters isolated so far obey the above-mentioned closed-shell superatomic rule. ${ }^{[14-19]}$ It is also noteworthy that in the case of group 11 clusters, both the whole cluster and its metal superatomic kernel possess a HOMO-LUMO gap for the considered "magic" electron count. Thus, the external "passivating" shell (the ligands and possibly additional outer metal atoms, all in their actual oxidation states) does not participate to the superatom (jellium) electron count.

Group-10 clusters of a certain size also tend to aggregate in a compact fashion. ${ }^{[28-32]}$ However, no general electron-counting rules developed for high nuclearity spherical clusters ${ }^{[4]}$ seem to apply to these species in a comprehensive manner. On one side, they often do not obey the classical Wade-Mingos rules. On the other side, the metal oxidation state being generally zero (or close to zero), their superatomic electron number is, at least at first sight, also zero (no valence $s$ electrons). Dahl's unique atom-precise $\mathrm{Pd}_{55}\left(\mathrm{PiPr}_{3}\right)_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}$ with a total of 614 valence electrons and zero $5 s$ electron (assuming $\operatorname{Pd}(0) 4 d^{10} 5 s^{0}$ configuration) is a typical example. Several questions arise from its structure and composition: (i) Are both the whole cluster and its isolated $\mathrm{Pd}_{55}$ kernel closed-shell entities? (ii) Is the number of 2-electron ligands, i.e., 32 , imposed by electronic stability or can it be varied without substantial stability and structural change? (iii) To what extent are the $4 d$ and $5 s$ metallic orbitals involved in the $\mathrm{Pd}-\mathrm{Pd}$ and Pd -ligand bonding? And finally, (iv) is the electronic structure of $\mathrm{Pd}_{55}\left(\mathrm{PiPr}_{3}\right)_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}$ somewhat related to that of group-11 superatoms? Density functional theory (DFT) calculations were carried out on the title compound, aiming at providing some answers to these questions. The main results are discussed here.

## Computational details

Density functional theory (DFT) calculations ${ }^{[33]}$ were performed using the Amsterdam Density Functional (ADF2016) code. ${ }^{[34]}$ Scalar relativistic effects were taken into account via the Zeroth Order Regular Approximation (ZORA).[35] The Vosko-WilkeNusair functional (VWN) ${ }^{[36]}$ for the Local Density Approximation (LDA) and gradient corrections for exchange and correlation of Becke and Perdew (BP86 functional), ${ }^{[77,38]}$ together with Grimme's empirical DFT-D3 corrections, ${ }^{[39]}$ were used for geometry optimization and analytical vibrational frequency computation. A triple-zeta basis set, augmented with a polarization function
(STO-TZP) ${ }^{[40]}$ for palladium was used. Similar results were obtained with other functionals (see SI). Natural atomic orbital (NAO) populations and Wiberg bond indices (WBIs) were computed using ADF optimized geometries with the natural bond orbital (NBO) 6.0 program, ${ }^{[44]}$ implemented in the Gaussain16 package, ${ }^{[42]}$ at the BP86/Def2-SVP ${ }^{[43]}$ level.

## Results and discussion

Three different $\mathrm{Pd}_{55} \mathrm{~L}_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}$ model clusters were considered in the calculations. The $\mathrm{PiPr}_{3}$ ligands of Dahl's compound were first modelized by simple $\mathrm{PH}_{3}$ phosphines to reduce computational efforts. However, because of the mismatch of the phosphine three-fold symmetry with the five-fold icosahedral symmetry axes, the exact symmetry of the computed cluster was reduced to $C_{2 h}$. Linear L = CO and CNH - the latter possesses electronic properties similar to those of phosphines and allows a higher symmetry of the molecule - ligands were also considered, for which the highest possible cluster symmetry is $I_{h}$. The three computed models provided similar results in terms of both their electronic structures and geometries overall. In the following, the $\mathrm{L}=\mathrm{CO}$ case is analyzed in more details. Since the ADF program does not work with the $I_{h}$ symmetry group, models with $L=C O$ and CNH were treated in $D_{5 d}$ symmetry although the optimized structures were found to be very close to $I_{h}$. This is why they are most often described below assuming ideal $I_{h}$ symmetry.

Table 1. Relevant atomic distances computed for the three optimized neutral models $\mathrm{Pd}_{55} \mathrm{~L}_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}\left(\mathrm{~L}=\mathrm{PH}_{3}, \mathrm{CO}, \mathrm{CNH}\right)$ in their triplet ground state configuration. The metal atom labelling corresponds to Pd'@Pd" ${ }_{12} @$ Pd"" ${ }_{42}$. Xray experimental distances of $\mathrm{Pd}_{55}\left(\mathrm{PiPr}_{3}\right)_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}$ are given for comparison. ${ }^{[1]}$

| $\left.\left[\mathrm{Pd}_{55 \mathrm{~L}}^{12} \text { ( } \mu_{3}-\mathrm{CO}\right)_{20}\right]\left(\mathrm{L}=\mathrm{PH}_{3}, \mathrm{CO}, \mathrm{CNH}\right)$ |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| L |  | $\mathrm{PH}_{3}$ | CO | CNH | Exp. ${ }^{[1]}$ |
| Average Distances (Å) | Pd'-Pd" | 2.636 | 2.649 | 2.645 | 2.63 |
|  | Pd'-Pd" | 2.772 | 2.785 | 2.782 | 2.76 |
|  | Pd"-Pd'" | 2.800 | 2.802 | 2.800 | 2.77 |
|  | Pd'"'-Pd'" | 2.845 | 2.857 | 2.853 | 2.83 |
|  | Pd'"'-L | 2.229 | 1.907 | 1.918 | 2.24 |
|  | Pd'"-CO | 2.092 | 2.096 | 2.092 | 2.07 |

The three $\mathrm{Pd}_{55} \mathrm{~L}_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}\left(\mathrm{~L}=\mathrm{PH}_{3}, \mathrm{CO}, \mathrm{CNH}\right)$ models were found to have a triplet ground state. (Table 1). The lowest singlet states were found to lie $0.83,0.45$ and 0.13 eV above the triplet for $\mathrm{L}=\mathrm{Ph}_{3}, \mathrm{CO}$ and CNH , respectively. The ground state optimized geometrical data are in a good agreement with the X ray data of $\mathrm{Pd}_{55}\left(\mathrm{P}^{\prime} \mathrm{Pr}_{3}\right)_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}{ }^{\left[{ }^{[1]}\right.} \mathrm{A}$ careful analysis of the Kohn-Sham frontier orbitals suggests that a closed-shell ground state configuration should be achieved with two additional electrons accompanied with minor structural differences with respect to their neutral states, i.e., pseudo- $I_{h}$ symmetry.

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Table 2. Relevant data computed for the three optimized dianionic models $\left[\mathrm{Pd}_{55} \mathrm{~L}_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}\right]^{2-}\left(\mathrm{L}=\mathrm{PH}_{3}, \mathrm{CO}, \mathrm{CNH}\right)$ in their ground state (singlet) configuration. The metal atom labeling corresponds to Pd'@Pd" ${ }_{12} @ P d^{\prime \prime \prime}$. The two different symmetry types of $\mathrm{Pd}^{\prime \prime \prime}$ atoms are labeled $\mathrm{Pd}_{\mathrm{a}}{ }^{\prime \prime \prime}$ and $\mathrm{Pd}_{\mathrm{b}}{ }^{\prime \prime \prime}$.

| $\left[\mathrm{Pd}_{55} \mathrm{~L}_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}\right]^{]^{--}}\left(\mathrm{L}=\mathrm{PH}_{3}, \mathrm{CO}, \mathrm{CNH}\right)$ |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| L |  | $\mathrm{PH}_{3}$ | CO | CNH |
| HOMO-LUMO gap (eV) |  | 0.54 | 0.58 | 0.62 |
| Average Distances ( $\AA$ ) [Wiberg indices] | Pd'-Pd" | 2.644 [0.078] | 2.658 [0.075] | 2.655 [0.074] |
|  | Pd"-Pd" | 2.781 [0.092] | 2.795 [0.092] | 2.792 [0.092] |
|  | Pd"-Pd'" | 2.798 [0.115] | 2.799 [0.112] | 2.798 [0.111] |
|  | Pd'"-Pd'" | 2.846 [0.069] | 2.858 [0.065] | 2.855 [0.067] |
|  | Pd'"'-L | 2.222 [0.475] | 1.898 [0.796] | 1.902 [0.766] |
|  | Pd'"'-CO | 2.089 [0.405] | 2.092 [0.398] | 2.091 [0.402] |
| Average NAO populations and atomic charges | $1 \times \mathrm{Pd}$ ' | $4 \mathrm{~d}^{9.33} 5 s^{0.92} 5 \mathrm{p}^{0.04}$ | $4 d^{9.35} 5 s^{0.95} 5 p^{0.05}$ | $4 d^{9.35} 5 s^{0.95} 5 p^{0.05}$ |
|  |  | -0.31 | -0.37 | -0.37 |
|  | $12 \times$ Pd" | $4 \mathrm{~d}^{9.48} 5 s^{0.63} 5 p^{0.03}$ | $4 \mathrm{~d}^{9.48} 5 \mathrm{~s}^{0.65} 5 \mathrm{p}^{0.03}$ | $4 d^{9.49} 5 s^{0.65} 5 p^{0.03}$ |
|  |  | -0.17 | -0.20 | -0.20 |
|  | $30 \times \mathrm{Pda}^{\prime \prime}{ }^{\prime \prime}$ | $4 \mathrm{~d}^{9.32} 5 \mathrm{~s}^{0.45} 5 \mathrm{p}^{0.01}$ | $4 d^{9.32} 5 s^{0.45} 5 p^{0.01}$ | $4 d^{9.32} 5 s^{0.45} 5 p^{0.01}$ |
|  |  | +0.21 | +0.21 | +0.22 |
|  | $12 \times$ Pdb ${ }^{\prime \prime \prime}$ | $4 d^{9.46} 5 s^{0.65} 5 p^{0.02}$ | $4 d^{9.29} 5 s^{0.69} 5 p^{0.02}$ | $4 d^{9.27} 5 s^{0.68} 5 p^{0.02}$ |
|  |  | -0.15 | -0.01 | +0.02 |
|  | $42 \times$ Pd"' (av.) | +0.11 | +0.15 | +0.16 |
|  | L | +0.20 | +0.01 | +0.02 |
|  | CO | -0.33 | -0.28 | -0.31 |

Calculations on the $\left[\mathrm{Pd}_{55} \mathrm{~L}_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}\right]^{2-}$ dianionic species confirmed this hypothesis, with significant HOMO-LUMO energy gaps of the order of $0.5-0.6 \mathrm{eV}$ (Table 2). As expected, the addition of two electrons hardly affects the interatomic distances of the cluster. The computed Pd-Pd Wiberg indices reflect the interatomic distances and are indicative of moderate metal-metal bonding interactions (Table 2). A glance at the computed natural atomic orbital (NAO) charges reveals some electron transfer from the $\mathrm{Pd}_{42}$ outer metal shell to the ligand envelope via $d \pi(\mathrm{Pd})-\pi^{*}(\mathrm{CO})$ back-bonding, as well as to the inner $\mathrm{Pd}_{12}$ shell and central Pd atom (Table 2). ${ }^{[1]}$

We discuss below the electronic structure of the $\left[\mathrm{Pd}_{55}\left(\mathrm{CO}_{12}\right)\left(\mu_{3}-\mathrm{CO}\right)_{20}\right]^{2-}$ dianion in more details, before returning to that of the neutral clusters. Its density of states (DOS), plotted in Figure 2, is consistent with a unique favoured closed-shell electron count of 616, corresponding to a dianionic species (similar DOS are computed for $\left[\mathrm{Pd}_{55}\left(\mathrm{PH}_{3}\right)_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}\right]^{2-}$ and $\left[\mathrm{Pd}_{55}(\mathrm{CNH})_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}\right]^{2-}$, see Figure S1 and S2 $\dagger$ ). A Kohn-Sham diagram of the frontier orbitals of $\left[\mathrm{Pd}_{55}\left(\mathrm{CO}_{12}\right)\left(\mu_{3}-\mathrm{CO}\right)_{20}\right]^{2-}$ is also provided in Figure 3. Unsurprisingly, the highest occupied states


Figure 2. Total, Pd , and $\mathrm{Pd}(5 s)$ projected DOS of $\left[\mathrm{Pd}_{55}(\mathrm{CO})_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}\right]^{2-}$ (Gaussian full width at half maximum $(0.1 \mathrm{eV})$. The dotted line corresponds to the energy of the HOMO
are of dominant $4 d$ metal character, while the lowest unoccupied ones have also some $\pi^{*}(\mathrm{CO})$ admixture.

A detailed analysis of the occupied orbital compositions reveals that ten of them are also of major $5 s(\mathrm{Pd})$ character. These orbitals are plotted in Figure 4. They can be easily identified as the 1S, 1P, 1D and 2S superatomic ("jellium") orbitals. The lowest
one (1S) is strongly bonding and lies below the whole block of the $4 d$ states. The highest one (2S) is still significantly bonding and situated 0.79 eV below the HOMO. Thus, with a $1 \mathrm{~S}^{2} 1 \mathrm{P}^{6} 1 \mathrm{D}^{10} 2 \mathrm{~S}^{2}$ configuration, $\left[\mathrm{Pd}_{55}\left(\mathrm{CO}_{12}\right)\left(\mu_{3}-\mathrm{CO}\right)_{20}\right]^{2-}$ is a 20 -electron superatom. Assuming that $\operatorname{Pd}(0)$ is $4 d^{10} 5 s^{0}$, one should expect only one of the $5 s$ combinations occupied by the two electrons associated with the -2 charge. Since ten $5 s$ combinations are actually occupied in the dianionic clusters, it means that nine $4 d$-type combinations have formally transferred their electrons to


Figure 3. Kohn-Sham molecular orbital (MO) diagram of $\left[\mathrm{Pd}_{55}\left(\mathrm{CO}_{12}\right)\left(\mu_{3}-\mathrm{CO}\right)_{20}\right]^{2-}$ ( $I_{h}$ symmetry assumed). Values in parenthesis indicate metal/ligand composition (in \%). Levels shown in red correspond to jellium levels. In $I_{h}$ symmetry, the vacant 1 F level is split into $t_{2 u}$ (LUMO) and $g_{u}$ (lying at higher energy and not shown).
nine of the 5 s combinations. In order to get a deeper understanding on this MO level crossing, we used the opportunity given by the ADF program suite to express the molecular orbitals as linear combinations of the orbitals of two fragments, that we chose to be $\left[\mathrm{Pd}_{55}\right]^{2-}$ metal kernel and its complete $\left[(\mathrm{CO})_{32}\right]$ ligand shell, respectively. Unsurprisingly, single-point spin-restricted calculations (as required by the ADF program) on the $\left[\mathrm{Pd}_{55}\right]^{2-}$ fragment could not be converged in a reasonable ground state. Excited states were obtained instead. Just to mention, the same situation occurred for the neutral $l_{n}$ fragment. These results are in line with calculations previously carried out on $\mathrm{Pt}_{55}$. ${ }^{[44]}$

Nevertheless, these results were sufficient for extracting the qualitative bonding picture sketched in Figure 5. For the sake of simplicity the $\pi^{*}(\mathrm{CO})$ orbitals are not considered in this diagram, although they play a substantial role in stabilizing the occupied $4 d$-block. The unstable $\left[\mathrm{Pd}_{55}\right]^{2-}$ fragment has $275(4 d)+10(5 s)=$ 285 low-lying combinations, of which $275+1=276$ are occupied.

Assuming formally that nine among the ten $5 s$ combinations are unoccupied, one is left with the $\left[\mathrm{Pd}_{55}\right]^{2-}$ MO picture shown on the left of Figure 5. The combinations of the ligand lone pair orbitals interact with the high-lying accepting orbitals on the metal


Figure 4. The ten occupied superatomic orbitals of $\left[\mathrm{Pd}_{55}\left(\mathrm{CO}_{12}\right)\left(\mu_{3}-\mathrm{CO}\right)_{20}\right]^{2-}$.
outer shell (sp-type), but also with the $4 d$-block. This later interaction results in the destabilization of nine $4 d$ combinations, which in turn transfer their electrons to the mainly unperturbed 1 P , 1D and $2 S$ orbitals. This creates a not-very-large but significant HOMO-LUMO gap which provides $\left[\mathrm{Pd}_{55}\left(\mathrm{CO}_{12}\right)\left(\mu_{3}-\mathrm{CO}\right)_{20}\right]^{2-}$ with a closed-shell configuration for the count of 20 superatom electrons. Unfortunately, because of important mixing with $\pi^{*}(\mathrm{CO})$ orbitals, it was not possible to individually identify the nine vacant $4 d$ combinations. However, a detailed orbital counting allows to determine their symmetry $\left(a_{g}+t_{1 u}+h_{g}\right)$, which is the same as that of the nine superatomic orbitals to which they transfer their electrons (Figure 5). To conclude this section, it is noteworthy that the two other computed models $\left[\mathrm{Pd}_{55} \mathrm{~L}_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}\right]^{2-}\left(\mathrm{L}=\mathrm{PH}_{3}\right.$, CNH ) provided the same electronic structure as $\left[\mathrm{Pd}_{55}\left(\mathrm{CO}_{12}\right)\left(\mu_{3}-\right.\right.$ $\left.\mathrm{CO})_{20}\right]^{2-}$.

A peculiarity of these $\left[\mathrm{Pd}_{55} \mathrm{~L}_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}\right]^{2-}$ clusters is that their (unstable) icosahedral $\mathrm{Pd}_{55}$ metal kernel needs its ligand outer shell for reaching a closed-shell configuration associated with a "magic" superatom electron count. A similar situation was found for another Pd cluster, namely the two-electron superatomic cuboctahedral species $\left[\mathrm{Pd}_{13}\left(\mu_{4}-\mathrm{C}_{7} \mathrm{H}_{7}\right)_{6}\right]^{2+.}{ }^{[45,46]}$ Our calculations on the $\left[\mathrm{Pd}_{55} \mathrm{~L}_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}\right]^{2-}$ models indicate that this closed-shell configuration is retained when the 12 terminal L ligands are removed, but with a very small HOMO-LUMO gap. Further adding of these 12 ligands results in a substantial

destabilization of the LUMOs, leading to the HOMO-LUMO gaps given in Table 2. We believe that the fact that some metal $d$-type orbitals participate to the bonding with the ligands (i.e., are destabilized and depopulated to the benefit of superatomic orbitals) is likely not to be uncommon in Pd or Pt cluster chemistry. Indeed, group-10 metals are at the borderline between middle transition-metal and group-11 elements that tend to keep their $d$ block fully occupied and non-bonding. Indeed, the general MO interacting diagram for


Figure 5. Simplified MO diagram of $\left[\mathrm{Pd}_{55}\left(\mathrm{CO}_{12}\right)(\mu 3-\mathrm{CO})_{20}\right]^{2-}$ obtained on the basis of the interaction between the $\left[\mathrm{Pd}_{55}\right]^{2-}$ and $[(\mathrm{CO})]_{32}$ fragments.
a closed-shell $\mathrm{Au}, \mathrm{Ag}$ or Cu superatom sketched in Figure 6 can be compared to that of Figure 5.

We now return to the discussion on the real charge of Dahl's cluster which is not a dianion, but a neutral species. Removing two electrons from the dianion does not modify the superatom electron count since the depopulated orbitals are $4 d$-type combinations (Figure 3). As said above, our computed species were found to have triplet ground state configurations. Unfortunately, no explicit mention of the spin state is provided in Dahl's paper for $\mathrm{Pd}_{55}\left(\mathrm{PiPr}_{3}\right)_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20} .{ }^{[1]}$ No paramagnetic behaviour can be traced from the reported ${ }^{31} \mathrm{P}$ NMR spectrum and unfortunately no NMR ${ }^{1} \mathrm{H}$ or ${ }^{13} \mathrm{C}$ measurements were reported. In any case, regardless of the considered spin state, Jahn-Teller instability is virtually cancelled by the very high cluster compactness of the cluster. Kinetic stability is also expected from the spin density plots of the computed $\mathrm{Pd}_{55} \mathrm{~L}_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}$ neutral models (Figure 7), which indicate that most of the spin density is confined in the heart of the metallic kernel, with negligible participation of the cluster surface shell (less than $6 \%$ ). Thus, low radical reactivity is expected for such species. In fact, another
fully characterized example of a 55 -atom MacKay superatom is known, namely the paramagnetic cluster $\left[\mathrm{Cu}_{43} \mathrm{Al}_{12}\right]\left(\mathrm{Cp}^{*}\right)_{12}\left(\mathrm{Cp}^{*}=\right.$ $\mathrm{C}_{5} \mathrm{Me}_{5}$ ) with an open-shell 67 -electron superatom configuration. ${ }^{[47]}$ The kinetic stability of the latter originates from the steric protection of a compact $\mathrm{Cp}^{*}$ outer shell. The not yet fully characterized Schmid's cluster (Nanogold(B) ${ }^{[48-52]} \mathrm{Au}_{55}\left(\mathrm{PPh}_{3}\right)_{12} \mathrm{Cl}_{6}$ is also (as well as its monoanion) an open-shell species with the $1 \mathrm{~S}^{2} 1 \mathrm{P}^{6} 1 \mathrm{D}^{10} 2 \mathrm{~S}^{2} 2 \mathrm{P}^{6} 1 \mathrm{~F}^{14} 1 \mathrm{G}^{9}$ superatomic configuration. ${ }^{[53]}$


Figure 6. Simplified general MO diagram for a ligated group-11 closed-shell $\left.\mid \mathrm{M}_{\mathrm{n}} \mathrm{L}_{\mathrm{p}}\right]^{(x-y)+}$ superatom with an arbitrarily chosen 20 -electron "magic" count for a direct comparison with the case of figure 5 . Ligands are considered as 2electron donors, with their formal charges adjusted accordingly (for example, neutral phosphines but anionic thiolates or halogenides).


Figure 7. Spin density plots of $\mathrm{Pd}_{55} \mathrm{~L}_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}$ with $\mathrm{L}=\mathrm{PH}_{3}(\mathrm{a}), \mathrm{CO}(\mathrm{b}), \mathrm{CNH}$ (c).

However, its chemical composition and electron count have been debated. ${ }^{[54]}$ Obviously, Mackay compact kernel structures of 55 atoms reaches a size where it starts to behave (somewhat) as a nanoparticle, allowing not a single but a (small) range of electron counts. The upper limit of this range corresponds to the best closed-shell favoured electron count, i.e., the "molecular" favoured count. Such a situation is not so uncommon in transitionmetal cluster chemistry. For example, it has been observed in the case of much smaller cobalt-carbonyl clusters. ${ }^{[55,56]}$ The fact that the neutral form of Dahl's cluster was isolated and not its closedshell dianion is likely to result from the balance of several factors, among which the method of synthesis is one of the most determinant. In any case, $\left[\mathrm{Pd}_{55} \mathrm{~L}_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}\right]$ should be easily be reduced.

## Conclusions

We have shown for the first time that the structure of the spherical nanosized cluster $\left[\mathrm{Pd}_{55} \mathrm{~L}_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}\right]$ can be interpreted using the jellium model as a regular superatom, characterized by the "magic" 20 -electron count ( $1 S^{2} 1 P^{6} 1 D^{10} 2 S^{2}$ configuration). Its open shell nature is associated with $4 d$-type single electrons located deeply on the metal kernel, so that the stability of the cluster is not affected. A favoured closed-shell situation occurs with two additional electrons (dianionic state). This does not modify the superatomic 20 -electron count. These 20 electrons are located in bonding combinations of 5 s AOs, which means that, considering the closed-shell dianion, nine 4d-type combinations have formally transferred their electrons in nine of the $5 s \mathrm{MO}$ combinations. This level crossing does not occur on the bare $\left[\mathrm{Pd}_{55}\right]^{2-}$ kernel. It necessitates the presence of the ligands, which destabilize the nine $4 d$-type MOs and open a HOMO-LUMO gap. This is at variance with group-11 ligated clusters for which no $d$-type to $s$ type electron transfer occurs. The need for the ligand envelope for inducing a closed-shell situation has already been noted in the case of the two-electron superatom species $\left[\mathrm{Pd}_{13}\left(\mu_{4}-\right.\right.$ $\left.\left.\mathrm{C}_{7} \mathrm{H}_{7}\right)_{6}\right]^{2+} \cdot{ }^{[45,46]}$

Interestingly, among the flurry of extraordinary diverse nanosized $\mathrm{CO} / \mathrm{PR}_{3}$-ligated icosahedral and $\mathrm{ccp} / \mathrm{hcp}$-based (homo/hetero) $\mathrm{Pd}_{\mathrm{n}}$ clusters reported over the last 20 years, ${ }^{[28,29]}$ only three conform to the icosahedral Mackay model, namely the title compound, the three-shell 145-metal-atom $\mathrm{Pd}_{145}(\mathrm{CO})_{\mathrm{x}}\left(\mathrm{PEt}_{3}\right)_{30}(\mathrm{x} \approx 60)$ cluster compound, ${ }^{[57]}$ and the $\mathrm{Pd}-\mathrm{Pt}$ four-shell 165 -metal-atom $\mathrm{Pd}_{164-\times \mathrm{Pt}_{\mathrm{x}}\left(\mu_{12}-\mathrm{Pt}\right)(\mathrm{CO})_{72}\left(\mathrm{PPh}_{3}\right)_{20}(\mathrm{x} \approx 7), ~(1)}$ cluster compound. ${ }^{[53]}$ It is likely that the superatom feature observed for $\mathrm{Pd}_{55} \mathrm{~L}_{12}\left(\mu_{3}-\mathrm{CO}\right)_{20}$ is a general rule that can be applicable to group-10 spherical or nearly spherical ligated clusters such as the $\mathrm{Pd}_{145}$ and $\mathrm{Pd} / \mathrm{Pt}_{165}$ species that contain interior two-shell icosahedral Mackay-type geometries. ${ }^{[57,58]}$ Following this line, we suggest that these palladium spherical clusters are indeed superatoms characterized by (at least approximately) "magic" electron counts, these electrons occupying $5 s(\mathrm{Pd})$ or $6 s(\mathrm{Pt})$ states and resulting from electron transfer from $4 d(\mathrm{Pd})$ or $5 d(\mathrm{Pt})$ states. We think that such electron transfers are likely to govern the metal-metal bonding in the whole chemistry of these group-10 clusters. Finally, note that the present
study is also relevant to catalysis as $\mathrm{Pd}_{55}$ clusters are close to the optimal cluster size for maximum catalytic activity of Pd clusters and small nanoparticle catalysts. ${ }^{[59-61]}$

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## Conflicts of interest

The authors declare no competing financial interest.
Keywords: Palladium nanocluster • Superatom • Mackay
icosahedron • Electronic structure -
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## FULL PAPER

DFT calculations show that the spherical Mackay icosahedral nanosized cluster $\mathrm{Pd}_{55}\left(\mathrm{PiPr}_{3}\right)_{12}\left(\mu_{3}-\right.$ $\mathrm{CO})_{20}$ can be considered as a regular 20-electron superatom.


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Theoretical analysis of the Mackay icosahedral cluster $\mathrm{Pd}_{55}\left(\mathrm{P}^{\mathrm{i}} \mathrm{Pr}_{3}\right)_{12}\left(\mu_{3}-\right.$ $\mathrm{CO})_{20}$ : An open-shell 20-electron superatom

