Cluster Core Isomerism Induced by Crystal Packing Effects in the [HCo15Pd9C3(CO)38]2– Molecular Nanocluster

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ABSTRACT: This article describes a rare case of cluster core isomerism in a large molecular organometallic nanocluster. In particular, two isomers of the [HCo15Pd9C3(CO)38]2– nanocluster, referred as TP-Pd and Oh-Pd, have been structurally characterized by single-crystal X-ray crystallography as their [NMe3(CH2Ph)]2[HCo15Pd9C3(CO)38]2CH2Cl2 (ca. 1:1 TP-Pd and Oh-Pd mixture), [NMe3(CH2Ph)]2[HCo15Pd9C3(CO)38]2CH2Cl2 (mainly TP-Pd), [NEt4][HCo15Pd9C3(CO)38]2CH2Cl2 (mainly TP-Pd), [MePPh3][HCo15Pd9C3(CO)38]2SCH2Cl2 (mainly TP-Pd), and [MePPh3][HCo15Pd9C3(CO)38]2(OH-Pd) salts. The cluster core of TP-Pd is a tricapped trigonal prism, whereas this is a tricapped octahedron in Oh-Pd. The presence in the solid state of the Oh-Pd or TP-Pd isomers depends on the cation employed and/or the number and type of co-crystallized solvent molecules. Often, mixtures of the two isomers, within the same single crystal or as mixtures of different crystals within the same crystallization batch, are obtained. Structural isomerism in organometallic nanoclusters is discussed and compared to that in Au–thiolate nanoclusters.

1. INTRODUCTION

Since the publication of the total structure of Au102(p-MBA)44 (p-MBA = p-mercaptobenzoic acid),1 a renewed interest for molecular metal nanoclusters arose, because of their relevance to ultrasmall metal nanoparticles, nanochemistry, and nanosciences.2–12 Thus, the structures of several Au, Ag, Cu, and bimetallic nanoclusters protected by thiolates, phosphines, selenolates, alkynyls, and other ligands have been determined by single-crystal X-ray diffractometry.13–19 The structures of these metal nanoclusters are dramatically influenced by the surface ligands. As a consequence, examples of cluster core isomerization phenomena induced by ligand substitution reactions have been documented.20,21 Even more intriguing is the case of Au134(PEt)44 (PET = phenylethanethiolate), for which two isomers differing in the cluster core structure, i.e., Au134Q and Au134P, have been crystallographically characterized. Au134P is less stable than Au134Q and is irreversibly converted into Au134Q by heating in toluene at 50 °C. This is the first and, at the moment, the only case of cluster core isomerism structurally documented for gold nanoclusters.22–23

The study of structural isomerism in metal nanoparticles by means of single-crystal X-ray crystallography is a very exciting but difficult task.25 Cluster core isomerism was documented for the first time in organometallic clusters, that is, [Pt6(μ3-PPh3)2Ph(PPh3)3]24–26 In the closed form, the Pt3 core of the cluster is an equilateral triangle, whereas it is an isosceles triangle with an elongated Pt–Pt open contact in the open form. Interestingly, the cluster core isomerism of [Pt6(μ3-PPh3)2Ph(PPh3)3] was a reversible phenomenon induced by the nature of the solvent and its co-crystallization effects.27,28 These results demonstrated for the first time that packing effects may induce changes in the structure of the core of small clusters. More recently, a peculiar case of cluster core isomerism, that is, dynamic permutational isomerism, has been reported in the closocluster [W2RhIr2(CO)9(η5-C5H5)]29 In this case, the two isomers differ for the relative positions (equatorial/axial) of the W and Ir atoms within the trigonal bipyramid structure of the cluster. Moreover, a dynamic equilibrium between the two isomers is present in solution, indicating that the cores of these clusters are not rigid.

Is it possible to have a dynamic and reversible isomerization of the core of larger clusters? This question is rather intriguing and related to the intimate rigid/deformable nature of the metal core of clusters of increasing sizes. To address this question, we have re-examined the structures of the [H3n−Co15Pd9C3(CO)38]n− (n = 0–3) molecular nanoclusters.30 These species may be reversibly interconverted by acid–base reactions, as summarized in Scheme 1. Their molecular structures were originally determined as their H3Co15Pd9C3(CO)38·2thf, [NEt4][H3Co15Pd9C3(CO)38]·0.5C6H14, [NMe3(CH2Ph)][HCo15Pd9C3(CO)38]·C6H14, and [NEt4][Co15Pd9C3(CO)38]·thf solids and salts. All of these clusters are composed of an inner Pd9(μ3-CO)2 core decorated on its surface by three square-pyramidal Co5C2(η5-C5HMe4)5 fragments. The most significant difference among the four [H3n−Co15Pd9C3(CO)38]n− (n = 0–3) clusters consisted

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in the fact that their Pd₉-kernel was a tricapped octahedron in [H₃Co₁₅Pd₉C₃(CO)₃₈]²⁻ and [H₂Co₁₅Pd₉C₃(CO)₃₈]⁻ (Oh-Pd₉ structure), whereas a distorted tricapped trigonal prism (TP-Pd₉ structure) was present in [HCo₁₅Pd₉C₃(CO)₃₈]²⁻ and [Co₁₅Pd₉C₃(CO)₃₈]³⁻ (Figure 1). The results previously reported indicated that reversible cluster core isomerism between the TP-Pd₉ and Oh-Pd₉ structures could be chemically induced by acid−base reactions. These results prompted us to prepare and structurally characterize the same [H₃₋ₙCo₁₅Pd₉C₃(CO)₃₈]ⁿ⁻ (n = 0−3) molecular nanoclusters with different cations and co-crystallization solvents, to verify whether the different structures adopted by the Pd₉-kernel was an intrinsic property of the differently charged anions (as originally speculated) or was due to different effects, such as packing forces and crystallization conditions. Surprisingly, we found that, at least for the dianion [HCo₁₅Pd₉C₃(CO)₃₈]²⁻ (Scheme 2), whereas a distorted tricapped trigonal prism (TP-Pd₉ structure) was present in [HCo₁₅Pd₉C₃(CO)₃₈]²⁻ and [Co₁₅Pd₉C₃(CO)₃₈]³⁻ (Figure 1). The results previously reported indicated that reversible cluster core isomerism between the TP-Pd₉ and Oh-Pd₉ structures could be chemically induced by acid−base reactions. 

These results prompted us to prepare and structurally characterize the same [H₃₋ₙCo₁₅Pd₉C₃(CO)₃₈]ⁿ⁻ (n = 0−3) anions with different cations and co-crystallization solvents, to verify whether the different structures adopted by the Pd₉-kernel was an intrinsic property of the differently charged anions (as originally speculated) or was due to different effects, such as packing forces and crystallization conditions. Surprisingly, we found that, at least for the dianion [HCo₁₅Pd₉C₃(CO)₃₈]²⁻, both the TP-Pd₉ and Oh-Pd₉ structures may be found in the solid state, depending on the counterion and/or co-crystallization solvents. Moreover, in some cases, both the cluster core isomers may be found in the same crystallization batch, as mixtures of different crystals or within the same crystal, suggesting that both isomers are present in solution or, at least, they are reciprocally interconverted during crystallization. This represents a genuine case of cluster core isomerism induced by packing forces in a larger molecular nanocluster. As an additional bonus of this study, the molecular structures of the new nanoclusters [Co₉Pd₄C₂(CO)₂₄]²⁻ and [Co₁₃Pd₃C₃(CO)₂₉]⁻ have been crystallographically determined.

2. RESULTS AND DISCUSSION

2.1. Synthesis. The synthetic protocol adopted in this work is very similar to that adopted and described in our previous paper. The major variation is represented by the exchange of the cation prior to the synthesis of [HCo₁₅Pd₉C₃(CO)₃₈]²⁻ and [Co₁₅Pd₉C₃(CO)₃₈]³⁻. Thus, [HCo₁₅Pd₉C₃(CO)₃₈]²⁻ was synthesized by reacting [NMe₃(CH₂Ph)]₂[Co₆C(CO)₁₅] and Pd(Et₂S)Cl₂ in thf according to the literature procedure. After workup, [NMe₃(CH₂Ph)]₂[Co₁₅Pd₉C₃(CO)₃₈] was extracted in dmf and the cation exchanged by adding a saturated solution of [CAT]X (CAT = NMe₃(CH₂Ph), NBu₄, NEt₃(CH₂Ph), MePPh₃; X = Cl, Br) in H₂O. The resulting [CAT]₂[HCo₁₅Pd₉C₃(CO)₃₈] was dissolved in CH₂Cl₂, resulting in [CAT]₂[HCo₁₅Pd₉C₃(CO)₃₈]·CH₂Cl₂. Slow diffusion of n-hexane on these solutions afforded crystals of [NMe₃(CH₂Ph)]₂[HCo₁₅Pd₉C₃(CO)₃₈]·CH₂Cl₂, [NMe₃(CH₂Ph)]₂[HCo₁₅Pd₉C₃(CO)₃₈]·2CH₂Cl₂, and [NMe₃(CH₂Ph)]₂[Co₁₅Pd₉C₃(CO)₃₈].

![Scheme 1. Reversible Interconversion of the [H₃₋ₙCo₁₅Pd₉C₃(CO)₃₈]ⁿ⁻ (n = 0−3) Molecular Nanoclusters by Means of Acid−Base Reactions](image-url)
[NEt₃(CH₂Ph)₂][HCo₁₅Pd₉C₃(CO)₃₈]·2CH₂Cl₂, [MePPh₃]₂[HCo₁₅Pd₉C₃(CO)₃₈]·2.5CH₂Cl₂, and [MePPh₃]₂[HCo₁₅Pd₉C₃(CO)₃₈] suitable for X-ray diffrac-tometry. All of these crystals contain the [HCo₁₅Pd₉C₃(CO)₃₈]²⁻ anion, whose structure was previously determined as its [NMe₃(CH₂Ph)]₂[HCo₁₅Pd₉C₃(CO)₃₈]·C₆H₁₄ salt, in which the Pd₉ core adopted a tricapped trigonal prismatic structure (TP-Pd₉). The same TP-Pd₉ structure was found in the new [NMe₃(CH₂Ph)]₂[HCo₁₅Pd₉C₃(CO)₃₈]·2CH₂Cl₂, [NEt₃(CH₂Ph)]₂[HCo₁₅Pd₉C₃(CO)₃₈]·2.5CH₂Cl₂, and [MePPh₃]₂[HCo₁₅Pd₉C₃(CO)₃₈]·2.5CH₂Cl₂ salts, even if in some cases traces of the Oh-Pd₉ isomer are present within the same crystals. Conversely, in the [MePPh₃]₂[HCo₁₅Pd₉C₃(CO)₃₈] salt, the Pd₉ core of the cluster dianion adopts an octahedral structure (Oh-Pd₉). Even more interestingly, a 1:1 mixture of the TP-Pd₉ and Oh-Pd₉ isomers of the [HCo₁₅Pd₉C₃(CO)₃₈]²⁻ anion is present in the [NMe₃(CH₂Ph)]₂[HCo₁₅Pd₉C₃(CO)₃₈]·CH₂Cl₂ salt. Moreover, often crystals containing different structures are obtained within the same batch, as, for instance, [NMe₃(CH₂Ph)]₂[HCo₁₅Pd₉C₃(CO)₃₈]·2CH₂Cl₂ (TP-Pd₉) and [NMe₃(CH₂Ph)]₂[HCo₁₅Pd₉C₃(CO)₃₈]·CH₂Cl₂ (Oh-Pd₉ and TP-Pd₉), or [MePPh₃]₂[HCo₁₅Pd₉C₃(CO)₃₈]·(Oh-Pd₉ and TP-Pd₉), and [MePPh₃]₂[HCo₁₅Pd₉C₃(CO)₃₈]·2.5CH₂Cl₂ (TP-Pd₉).

It must be remarked that, in the attempt to isolate [NBu₄]⁺ salts of [HCo₁₅Pd₉C₃(CO)₃₈]²⁻ in accord with the same procedure, crystals of [NBu₄]₂[Co₈Pd₄C₂(CO)₂₄] were obtained instead. This indicates that the reaction of [NBu₄]₄[H₂Co₂₀Pd₁₆C₄(CO)₄₈] with HBF₄·Et₂O, under the conditions described above, has an outcome completely different compared to that of salts with different cations. It is likely that this is due to solubility issues of the starting clusters and reaction intermediates as a function of the cation. Indeed, the [NBu₄]⁺ salts of anionic metal carbonyl clusters are usually far more soluble than salts of the same cluster anions with other ammonium or phosphonium cations.

[CAT]₃[Co₁₅Pd₉C₃(CO)₃₈] was, then, obtained by reducing the amount of HBF₄·Et₂O in the acetone solution employed in the above-mentioned synthetic protocol, or by treating the CH₂Cl₂ solution of [CAT]₂[HCo₁₅Pd₉C₃(CO)₃₈] with a strong base. Slow diffusion of n-hexane on these solutions afforded crystals of [NET₃(CH₂Ph)]₂[HCo₁₅Pd₉C₃(CO)₃₈]·CH₂Cl₂ and [MePPh₃]₂[HCo₁₅Pd₉C₃(CO)₃₈]·CH₂Cl₂. In these cases, the structures of the trianions were analogous to that previously reported as the [NET₄]₃[Co₁₅Pd₉C₃(CO)₃₈]·thf salt (TP-Pd₉). Conversely, by adding further HBF₄·Et₂O to the CH₂Cl₂ solution of [CAT]₂[HCo₁₅Pd₉C₃(CO)₃₈], the species [CAT]-[H₂Co₁₅Pd₉C₃(CO)₃₈] was formed as evidenced by IR spectroscopy. This, in turn, was converted into H₃Co₁₅Pd₉C₃(CO)₃₈ during crystallization in the presence of an excess of HBF₄·Et₂O. In the attempt to obtain new crystal salts of [CAT]·H₂Co₁₅Pd₉C₃(CO)₃₈ and

**Figure 2.** Molecular structures of the [HCo₁₅Pd₉C₃(CO)₃₈]²⁻ anion as found in [NMe₃(CH₂Ph)]₂[HCo₁₅Pd₉C₃(CO)₃₈]·CH₂Cl₂ (1), (a) Oh-Pd₉ isomer and (b) TP-Pd₉ isomer (isomer ratio within the crystal 1:1); (c) [NMe₃(CH₂Ph)]₂[HCo₁₅Pd₉C₃(CO)₃₈]·2CH₂Cl₂ (2) TP-Pd₉ isomer; (d) [NET₃(CH₂Ph)]₂[HCo₁₅Pd₉C₃(CO)₃₈]·CH₂Cl₂ (3), TP-Pd₉ isomer; (e) [MePPh₃]₂[HCo₁₅Pd₉C₃(CO)₃₈]·2.5CH₂Cl₂ (5), TP-Pd₉ isomer; (f) [MePPh₃]₂[HCo₁₅Pd₉C₃(CO)₃₈]·CH₂Cl₂ (7), Oh-Pd₉ isomer. (Orange, Pd; blue, Co; red, O; gray, C). Side (left) and top (right) views are given for each molecule.
H_3Co_15Pd_9C_3(CO)_38, the whole procedure was repeated several times by further increasing the amount of the acid employed. Even if this was unsuccessful, when a very large excess of HBF_4·Et_2O was employed, a few crystals of the [NMe_3(CH_2Ph)]_2[HCo_15Pd_9C_3(CO)_38]·CH_2Cl_2 salt were obtained. These contain the new [Co_13Pd_3C_3(CO)_29]− cluster anion that, probably, is a decomposition product of [H_3nCo_15Pd_9C_3(CO)_38]n− (n = 0–3).

2.2. Molecular Structures of the Two Isomers of [HCo_15Pd_9C_3(CO)_38]−. In this section, the structure of [HCo_15Pd_9C_3(CO)_38]− determined in the [NMe_3(CH_2Ph)]_2[HCo_15Pd_9C_3(CO)_38]·CH_2Cl_2 (1) salt were obtained. These contain the new [Co_13Pd_3C_3(CO)_29]− cluster anion that, probably, is a decomposition product of [H_3nCo_15Pd_9C_3(CO)_38]n− (n = 0–3).

Figure 3. Pd_9 cores of [HCo_15Pd_9C_3(CO)_38]− as found in different salts. The structures in the same line have been found within the same crystal. [NMe_3(CH_2Ph)]_2[HCo_15Pd_9C_3(CO)_38]·CH_2Cl_2 (1): (a) Oh-Pd_9 isomer (molecule 1), (b) TP-Pd_9 isomer (91% of molecule 2), and (c) Oh-Pd_9 isomer (9% of molecule 2). [NMe_3(CH_2Ph)]_2[HCo_15Pd_9C_3(CO)_38]·2CH_2Cl_2 (2): (d) TP-Pd_9 isomer. [NMe_3(CH_2Ph)]_2[HCo_15Pd_9C_3(CO)_38]·CH_2Cl_2 (3): (e) TP-Pd_9 isomer (94%), (f) Oh-Pd_9 isomer (6%). [MePPh_3]_2[HCo_15Pd_9C_3(CO)_38]·2.5CH_2Cl_2 (5): (g) TP-Pd_9 isomer. [MePPh_3]_2[HCo_15Pd_9C_3(CO)_38] (7): (h) Oh-Pd_9 isomer. H_3Co_15Pd_9C_3(CO)_38, the whole procedure was repeated several times by further increasing the amount of the acid employed. Even if this was unsuccessful, when a very large excess of HBF_4·Et_2O was employed, a few crystals of the [NMe_3(CH_2Ph)]_2[HCo_15Pd_9C_3(CO)_38]·CH_2Cl_2 salt were obtained. These contain the new [Co_13Pd_3C_3(CO)_29]− cluster anion that, probably, is a decomposition product of [H_3nCo_15Pd_9C_3(CO)_38]n− (n = 0–3).

2.2. Molecular Structures of the Two Isomers of [HCo_15Pd_9C_3(CO)_38]−. In this section, the structure of [HCo_15Pd_9C_3(CO)_38]− determined in the [NMe_3(CH_2Ph)]_2[HCo_15Pd_9C_3(CO)_38]·CH_2Cl_2 (1) contains two independent cluster anion molecules within the asymmetric unit of the unit cell, one displaying a TP-Pd_9 core and the other an Oh-Pd_9 core. Moreover, some crystallographic disorder has been found in the metal core of the former molecule, which can be better described as 91% TP-Pd_9 and 9% Oh-Pd_9. Figure 3. Pd_9 cores of [HCo_15Pd_9C_3(CO)_38]− as found in different salts. The structures in the same line have been found within the same crystal. [NMe_3(CH_2Ph)]_2[HCo_15Pd_9C_3(CO)_38]·CH_2Cl_2 (1): (a) Oh-Pd_9 isomer (molecule 1), (b) TP-Pd_9 isomer (91% of molecule 2), and (c) Oh-Pd_9 isomer (9% of molecule 2). [NMe_3(CH_2Ph)]_2[HCo_15Pd_9C_3(CO)_38]·2CH_2Cl_2 (2): (d) TP-Pd_9 isomer. [NMe_3(CH_2Ph)]_2[HCo_15Pd_9C_3(CO)_38]·CH_2Cl_2 (3): (e) TP-Pd_9 isomer (94%), (f) Oh-Pd_9 isomer (6%). [MePPh_3]_2[HCo_15Pd_9C_3(CO)_38]·2.5CH_2Cl_2 (5): (g) TP-Pd_9 isomer. [MePPh_3]_2[HCo_15Pd_9C_3(CO)_38] (7): (h) Oh-Pd_9 isomer. H_3Co_15Pd_9C_3(CO)_38, the whole procedure was repeated several times by further increasing the amount of the acid employed. Even if this was unsuccessful, when a very large excess of HBF_4·Et_2O was employed, a few crystals of the [NMe_3(CH_2Ph)]_2[HCo_15Pd_9C_3(CO)_38]·CH_2Cl_2 salt were obtained. These contain the new [Co_13Pd_3C_3(CO)_29]− cluster anion that, probably, is a decomposition product of [H_3nCo_15Pd_9C_3(CO)_38]n− (n = 0–3).
(d) \(\text{[MePPh}_3\text{]}\text{[HCO}_{10}\text{Pd}_9\text{C}_3\text{(CO)}_{38}]\cdot 2.5\text{CH}_2\text{Cl}_2\) (5) displays a TP-Pd\(_9\) core.

(e) \(\text{[MePPh}_3\text{]}\text{[HCO}_{10}\text{Pd}_9\text{C}_3\text{(CO)}_{38}]\) (7) displays a perfectly ordered Oh-Pd\(_9\) core.

(f) The previously reported \(\text{[NMe}_3\text{(CH}_2\text{Ph)}\text{]}_2\cdot \text{[HCO}_{10}\text{Pd}_9\text{C}_3\text{(CO)}_{38}]\cdot \text{C}_6\text{H}_{14}\) salt displayed a TP-Pd\(_9\) core.\(^{30}\)

We can remark the following points:

(i) Within the same crystal structure (1), an almost equimolular mixture of the two isomers is present.

(ii) A small amount of the Oh isomer (ca. 6%) is present in (3), which otherwise displays a TP core (94%).

(iii) All of the salts reported contain the \([\text{NMe}_3\text{(CH}_2\text{Ph)}\text{]}^+, [\text{NET}_3\text{(CH}_2\text{Ph)}\text{]}^+, \text{or [MePPh}_3\text{]}^+\) cations and have been crystallized from \(\text{CH}_2\text{Cl}_2/n\)-hexane. The different Oh/TP structures displayed in the solid state by the \(\text{[HCO}_{10}\text{Pd}_9\text{C}_3\text{(CO)}_{38}]^2-\) anion seem to depend on the cation as well as the number of co-crystallized solvent molecules.

(iv) Mixtures of crystals of (1)/(2) and (5)/(7) are often obtained in the same crystallization batches.

(v) In the case of the \(\text{[MePPh}_3\text{]}_2\text{[HCo}_{15}\text{Pd}_9\text{C}_3\text{(CO)}_{38}]\cdot x\text{CH}_2\text{Cl}_2\) salts, the cluster displays the TP-Pd\(_9\) structure when \(x = 2.5\) (5), and the Oh-Pd\(_9\) structure when \(x = 0\) (7).

(vi) Similarly, for \(\text{[NMe}_3\text{(CH}_2\text{Ph)}\text{]}_2\text{[HCo}_{15}\text{Pd}_9\text{C}_3\text{(CO)}_{38}]\) salts, the TP-Pd\(_9\) structure is displayed when solv = \(\text{C}_6\text{H}_{14}\) or \(2\text{CH}_2\text{Cl}_2\) (2), whereas a 1:1 mixture of the TP-Pd\(_9\) and Oh-Pd\(_9\) structures is found when solv = \(\text{CH}_2\text{Cl}_2\) (1).

The main bond distances of \(\text{[HCO}_{10}\text{Pd}_9\text{C}_3\text{(CO)}_{38}]^2-\) as found in the different salts are listed in Table 1, whereas Table 2 reports the numbers of M-M bonds and CO ligands grouped by categories for the same compounds. For the sake of completeness, analogous data for the \(\text{[Co}_{10}\text{Pd}_9\text{C}_3\text{(CO)}_{38}]^{3-}\)trianion are compiled in Tables S.1 and S.2 of the Supporting Information. It must be remarked that the structure of the trianion has been determined as the \(\text{[NMe}_3\text{(CH}_2\text{Ph)}\text{]}_3^-, [\text{NET}_3\text{(CH}_2\text{Ph)}\text{]}_3^-, \text{or [MePPh}_3\text{]}_3^-\) anion.\(^{32}\)

As a general comment, by considering all of the data reported in Tables 1, 2, S.1 and S.2, as well as those reported in the previous article for the different \(\text{[H}_n\text{Co}_{10}\text{Pd}_9\text{C}_3\text{(CO)}_{38}]^m-\) \((n = 0−3)\) clusters,\(^{30}\) all of the bonding parameters depend solely on the structure adopted by the Pd\(_9\) core (TP or Oh) and not on the overall charge of the clusters. This is likely to be due to the fact that, in such large molecular clusters, the anionic net negative charge is delocalized over the entire molecule.

Regarding the Co–C\(_{\text{carbide}}\), Pd–C\(_{\text{carbide}}\) and Co–Co bonding contacts, these are almost identical for what concerns their number and distances in all of the compounds considered, regardless of the structure adopted by the Pd\(_9\)

### Table 1: Average bond distances (Å) for \(\text{[HCo}_{15}\text{Pd}_9\text{C}_3\text{(CO)}_{38}]^{2-}\) as Found in Different Salts \(^a,b,c,d,e,f\)

| n   | 1-TP  | 1-Oh  |
|-----|-------|-------|
| 1   |       |       |
| Co–Co | 2.49(3) | 2.77(4) |
| Pd–Co | 2.64(3) | 3.02(4) |
| Pd–Pd | 2.64(3) | 3.02(4) |
| Co–Pd | 2.65(3) | 3.02(4) |
| Cl–Pd | 2.57(2) | 2.97(3) |

\(^a\) Data collected at 100 K. \(\text{[MePPh}_3\text{]}_2\text{[HCo}_{15}\text{Pd}_9\text{C}_3\text{(CO)}_{38}]\cdot 2\text{CH}_2\text{Cl}_2.\)

\(^b\) \(\text{[NMe}_3\text{(CH}_2\text{Ph)}\text{]}_2\text{[HCo}_{15}\text{Pd}_9\text{C}_3\text{(CO)}_{38}]\cdot 2\text{CH}_2\text{Cl}_2.\)

\(^c\) \(\text{[NMe}_3\text{(CH}_2\text{Ph)}\text{]}_3^-\)–\(\text{[HCo}_{15}\text{Pd}_9\text{C}_3\text{(CO)}_{38}]^{2-}\)–\(\text{[CH}_2\text{Cl}_2]_2.\)

\(^d\) \(\text{[MePPh}_3\text{]}_2\text{[HCo}_{15}\text{Pd}_9\text{C}_3\text{(CO)}_{38}]\cdot 3\text{CH}_2\text{Cl}_2.\)

\(^e\) \(\text{[NMe}_3\text{(CH}_2\text{Ph)}\text{]}_3^-\)–\(\text{[HCo}_{15}\text{Pd}_9\text{C}_3\text{(CO)}_{38}]^{2-}\)–\(\text{[MePPh}_3\text{]}_3^-\).
Table 2. Numbers of M–M Bonds and CO Ligands Grouped by Categories for [HCo15Pd9C3(CO)38]2− as Found in Different Saltsa,b,c,d,e,f

| salt                  | 1-Oh | 1-TP | 2   | 3   | 5   | 7   |
|-----------------------|------|------|-----|-----|-----|-----|
| Pd(μ3)-core type      | Oh   | TP   | TP  | TP  | TP  | Oh  |
| M–M                   | 74   | 69   | 68  | 66  | 68  | 72  |
| Co–Co                 | 24   | 24   | 24  | 24  | 24  | 24  |
| Co–Pd                 | 29   | 26   | 26  | 23  | 25  | 28  |
| Pd–Pd                 | 21   | 19   | 18  | 19  | 19  | 20  |
| Co–C(carbide)         | 15   | 15   | 15  | 15  | 15  | 15  |
| Pd–C(carbide)         | 3    | 3    | 3   | 3   | 3   | 3   |
| μ-CO                  | 10 (Co–Co) | 9 (Co–Co) | 8 (Co–Co) | 10 (Co–Co) | 10 (Co–Co) | 9 (Co–Co) |
| μ2-CO                 | 9 (Co–Pd) | 10 (Co–Pd) | 10 (Co–Pd) | 9 (Co–Pd) | 10 (Co–Pd) | 9 (Co–Pd) |
| μ3-CO                 | 2 (Pd3) | 2 (Pd3) | 2 (Pd3) | 2 (Pd3) | 2 (Pd3) | 2 (Pd3) |
| t-CO                  | 17   | 16   | 17  | 17  | 16  | 18  |

aData collected at 100 K. b[(1) [NMMe3(ChaPh)][HCo15Pd9C3(CO)38]·CH2Cl2. (2) [NMMe3(ChaPh)][HCo15Pd9C3(CO)38]·2CH2Cl2. c[(3) [NET3(ChaPh)][HCo15Pd9C3(CO)38]·CH2Cl2. d[(5) [MePPh3][HCo15Pd9C3(CO)38]·2.5CH2Cl2. e[(7) [MePPh3][HCo15Pd9C3(CO)38].

core, the charge of the cluster, the counterion, and co-crystallization solvent molecules. The organometallic Co5-C-(CO)12 fragments that decorate and stabilize the surface of such clusters retain the same square-pyramidal structure in all of the species structurally investigated, apart from some minor differences in the stereochemistry of the CO ligands. Overall, each carbide atom is encapsulated within an octahedral Co5Pd3C cage.

The Pd–Pd bonds display similar average values in all of the clusters, but systematically the clusters adopting an Oh-Pd9 structure show more Pd–Pd bonding contacts (20–21) than those with a TP-Pd9 structure (18–19). We should expect 21 Pd–Pd bonds for both regular tricapped TP-Pd9 and Oh-Pd9 structures. The latter ones indeed always display almost regular structures and follow this rule. Conversely, in the case of the clusters with a TP-Pd9 core, the structures are distorted and the three capping Pd atoms usually form three and not four Pd–Pd bonds.

The number of Co–Pd contacts that can be considered as bonds is always greater in the clusters with a Oh-Pd9 core (28–30 contacts) than the TP-Pd9 (20–21) that those with a TP-Pd9 core (23–26 bonds). At the same time, the average Co–Pd bonding distances are greater in the Oh-Pd9 clusters than in the TP-Pd9 clusters. We can envision some kind of compensation mechanism, in the sense that passing from the Oh-Pd9 isomer to the TP-Pd9 isomer the number of Co–Pd bonds is reduced but their strength (as indicated by their average distances) is increased.

Idealized TP and Oh structures differ by a 60° twist of two opposite triangles about a 3-fold axis. The twist angle can be assumed to be 0° for a regular TP and 60° for a regular Oh. By analyzing all of the crystal structures reported in this article, it appears that such twist angle is 12–14° for the clusters displaying the TP-Pd9 structure and 61–64° for the Oh-Pd9 isomers, quite close to the idealized values. None of the structures so far determined adopts a twist angle intermediate between these two values. Therefore, we can speculate that the TP-Pd9 and Oh-Pd9 structures represent two separate energy minima; otherwise, structures with intermediate twist angles should have formed.

To shed light on this point, the energies of two [Co5Pd3C3(CO)18]3− structures derived from the X-ray data obtained for TP-Pd9 and Oh-Pd9 isomers of [HCo15Pd9C3(CO)38]2− were compared using the PBEh-3c method (the hydride atom was not preliminarily included, since it was not crystallographically located). The TP-Pd9 isomer was more stable by about 16 kcal mol−1 with respect to the Oh-Pd9 isomer, in agreement with the fact that the TP-Pd9 structure was the only one experimentally found for the trianion [Co10Pd3C3(CO)38]3−. It is, however, worth noting the roles of crystal packing, cations, and solvent molecules are not accounted. To make the model structures more similar from an electronic point of view to the real compounds, a hydrogen atom (formally as H+) was placed in the center of the clusters. The TP-Pd9 structure remains also in this case the most favorable by about 18 kcal mol−1. These preliminary calculations suggest a key role of the position of the hydride in the relative stability of the clusters and perhaps in the isomerization process. Thus, the interconversion of the TP-Pd9 and Oh-Pd9 isomers cannot imply a simple reciprocal rotation of two Pd3 triangles but must require a more complex mechanism, probably involving also hydride migration within the metal cage of the cluster. Because of the large size and complexity of such clusters, it is not possible to perform more advanced computational investigations on the possible mechanisms for the formation and/or interconversion of the two isomers, including optimization of the position of the hydride atom. Moreover, high-nuclearity carbonyl nanoclusters such as [HCo15Pd9C3(CO)38]3− display almost featureless and identical UV-visible spectra, hampering further experimental studies on the isomerization process in solution.

Regarding the ionic packings of the different salts, only normal van der Waals contacts are present within the unit cells among the cluster anions, organic cations, and co-crystallized solvent molecules. There is no evidence of particular interactions that might favor the TP-Pd9 or Oh-Pd9 isomers. Thus, the presence of one or the other isomer (or a mixture of both) within a single cluster should be due to a subtle balance of inter- and intra-molecular interactions, which cannot be predicted a priori. This gives a further support to our hypothesis that both isomers are present in solution. Then, weak packing forces due to the cations and/or co-crystallized solvent molecules may favor the crystallization of one or the other isomer, or a mixture of both.

2.3. Molecular Structure of [Co15Pd9C3(CO)29]−. The molecular structure of [Co15Pd9C3(CO)29]− has been determined as [NMMe3(ChaPh)][Co15Pd9C3(CO)29]·CH2Cl2 (Figure 4, Tables S.3 and S.4). The cluster is...
composed of a Co$_{13}$Pd$_3$C$_3$ kernel stabilized on its surface by 29 CO ligands. The average diameter of the Co$_{13}$Pd$_3$C$_3$ core is 0.7 nm and, including the carbonyl ligands, the average diameter of the whole molecule is 1.2 nm. The cluster may be partitioned into an inner triangular Pd$_3$ unit bonded to a Co(CO)$_4$ and a Co$_{12}$C$_3$(CO)$_{25}$ fragment. The latter formally arises from the condensation of three square-pyramidal Co$_5$C units sharing three vertices. An inner triangular Pd$_3$ unit is present also in the [Os$_{18}$Pd$_3$C$_2$(CO)$_{48}$]$^{2-}$ cluster, where the Pd 3 core is bonded to two Os 9 C(CO)$_{24}$ fragments. These [Os$_{18}$Pd$_3$C$_2$(CO)$_{48}$]$^{2-}$ and [Co$_{13}$Pd$_3$C$_3$(CO)$_{29}$]$^{-}$ clusters, as well as the parent [H$_{16}$Co$_{15}$Pd$_9$C$_3$(CO)$_{38}$]$^{2-}$ and [H$_{6-n}$Co$_{20}$Pd$_{16}$C$_4$(CO)$_{48}$]$^{(n=3\cdots6)}^{2-}$, may be viewed as Pd$_n$ clusters stabilized by Co and Os organometallic fragments.

The carbide atoms are enclosed within octahedral Co$_9$PdC cages. [Co$_{13}$Pd$_3$C$_3$(CO)$_{29}$]$^{-}$ is the second example of a metal carbonyl cluster containing three isolated carbide atoms, [HCo$_{16}$Pd$_3$C$_3$(CO)$_{38}$]$^{5-}$ being the first one. Conversely, [Ni$_{11}$C$_3$(C)(CO)$_4$(AuPPh$_3$)$_3$]$^{-}$ presented one carbide and a C$_2$-acetylide unit.

2.4. Molecular Structure of [Co$_8$Pd$_4$C$_2$(CO)$_{24}$]$^{2-}$. The molecular structure of the new [Co$_8$Pd$_4$C$_2$(CO)$_{24}$]$^{2-}$ cluster has been determined as its [NBu$_4$]$_2$[Co$_8$Pd$_4$C$_2$(CO)$_{24}$] salt. The structure of [Co$_8$Pd$_4$C$_2$(CO)$_{24}$]$^{2-}$ is very similar to that of the previously reported [Co$_8$Pt$_4$C$_2$(CO)$_{24}$]$^{2-}$ (Figure 6). For the sake of comparison, the crystal structure of the isomorphous [NBu$_4$]$_2$[Co$_8$Pt$_4$C$_2$(CO)$_{24}$] salt is included in this work. The Co$_8$M$_4$ (M = Pd, Pt) core of these clusters is a face-sharing trioctahedron (Figure 7). The two carbide atoms are located in the outer octahedra. The stereochemistry of the CO ligands is the same in both clusters, with 12 terminal and 12 edge-bridging carbonyls. The major difference between [Co$_8$Pd$_4$C$_2$(CO)$_{24}$]$^{2-}$ and [Co$_8$Pt$_4$C$_2$(CO)$_{24}$]$^{2-}$ is related to the location of the four Pd and Pt atoms. The metal atoms of [Co$_8$Pd$_4$C$_2$(CO)$_{24}$]$^{2-}$ are perfectly ordered, and the four Pd atoms are located on the two internal triangles, two per each triangle in a relative pseudo-trans position. Conversely, the four Pt atoms of [Co$_8$Pt$_4$C$_2$(CO)$_{24}$]$^{2-}$ are disordered on the same two internal triangles of the metal cage.

Figure 4. (a) Molecular structure of [Co$_{13}$Pd$_3$C$_3$(CO)$_{29}$]$^{-}$ (orange, Pd; blue, Co; red, O; gray, C). (b) [Co$_{13}$Pd$_3$C$_3$] core represented with a color code that emphasizes its formal building-up: the three Co$_5$C units are represented in different colors (blue, yellow, and green for Co) and shared atoms are bicolored. The unique Co of Co(CO)$_4$ is represented in purple and Pd atoms in orange.

Figure 5. (Top) Chemical interconversion of the [H$_{16}$Co$_{15}$Pd$_9$C$_3$(CO)$_{38}$]$^{2-}$, [HCo$_{16}$Pd$_3$C$_3$(CO)$_{38}$]$^{5-}$, and [Co$_{13}$Pd$_3$C$_3$(CO)$_{29}$]$^{-}$ clusters by oxidation with strong acids. (Bottom) Structural relationship among their close-packed Pd$_{16}$ (ABC, 3 + 6 + 7), Pd$_9$ (AB, 3 + 6), and Pd$_3$ (A, 3) cores.
nanoclusters, or their in packing forces usually do not a obtained. This is quite surprising, since weak intermolecular be a tricapped octahedron (Oh-Pd9) or a tricapped trigonal raphy as several di isomers, within the same single crystal or as mixtures of their structures determined by single-crystal X-ray crystallography. Different structural isomers found in Au−thiolate and organometallic (carbonyl) molecular nanoclusters have been isolated and/or the number and type of co-crystallized solvent molecules. Often, mixtures of the two depends on the cation employed and/or the number and type of co-crystallized solvent molecules. A related surface ligand isomerism has been documented also for organometallic nanoclusters, and in particular in the case of cobalt and nickel carbide carbonyl clusters decorated on the surface by [AuPPh3]+ fragments.34,37,38

Despite the different nature of the metals and ligands involved in Au−thiolate and organometallic (carbonyl) molecular nanoclusters, there seems to be some general structural analogies among these categories of atomic precise nanoclusters.28,39,40 These analogies somehow regard the isomerization and dynamic behavior of their metal cores, as well as the protective and adaptive nature of the staple motives or ligand shells. As our understanding of the intimate total structures of metal nanoparticles is increasing, by watching them with the eye of molecular chemistry, concepts, which have been well consolidated along the years in coordination and organometallic chemistry, find their application also to describe metal nanoparticles.

4. EXPERIMENTAL SECTION

4.1. General Procedures. All reactions and sample manipulations were carried out using standard Schlenk techniques under nitrogen and in dried solvents. All of the reagents were commercial products (Aldrich) of the highest purity available and used as received, except [NMMe3(CH2Ph)]2[Co6C(CO)15]44 and PdCl2(ET3S)2, which were prepared according to the literature.45 IR spectra were recorded on a PerkinElmer Spectrum One interferometer in CaF2 cells. Structure drawings have been performed with SCHAKAL99.46

4.2. Synthesis of [CAT]2[HCo15Pd9C3(CO)38] (CAT = NMe3(CH2Ph), NBu4, NET3(CH2Ph), and MePPh3). Solid PdCl2(ET3S)2 (0.932 g, 2.90 mmol) was added in small portions to a solution of [NMMe3(CH2Ph)]2[Co6C(CO)15]1 (1.37 g, 1.27 mmol) in THF (20 mL) over a period of 2 h. After stirring the mixture at room temperature for 2 d, the solvent was removed under reduced pressure. The residue was then, washed with H2O (2 × 20 mL) and toluene (2 × 20 mL), and [NMMe3(CH2Ph)]2[HCo15Pd9C3(CO)38] extracted in dmf (15 mL). The cation was exchanged by adding a saturated solution of [CAT]X (CAT = NMe3(CH2Ph), NBu4, NET3(CH2Ph), and MePPh3) X = Cl, Br in H2O (30 mL), and the precipitation of [CAT]2[HCo15Pd9C3(CO)38] was completed by addition of H2O (50 mL). The resulting solid was recovered by filtration, washed with H2O (2 × 20 mL), and vacuum-dried. [CAT]4[H2Co20Pd16C4(CO)48] was dissolved in acetone (30 mL) and treated with HBF4·Et2O (500 µL, 3.62 mmol). After 10 min, the solvent was removed in vacuo and the residue dissolved in CH2Cl2 (20 mL) and filtered. The solution was eventually layered with n-hexane (40 mL), affording single crystals of [NMMe3(CH2Ph)]2·[HCo15Pd9C3(CO)38]·CH2Cl2, [NMMe3(CH2Ph)]2·[HCo15Pd9C3(CO)38]·2CH2Cl2, [NET3(CH2Ph)]2·[HCo15Pd9C3(CO)38]·CH2Cl2, [MePPh3]2·[HCo15Pd9C3(CO)38]·[HCo15Pd9C3(CO)38]·CH2Cl2, [MePPh3]2·[HCo15Pd9C3(CO)38]·2CH2Cl2, and [MePPh3]2·[HCo15Pd9C3(CO)38] (yields based on Pd 45−55%). When [CAT]+ = [NBu4]+, crystals of [NBu4]2·[CoPd2C2(CO)24] were obtained following the same procedure. [CAT]4[H2Co20Pd16C4(CO)48] IR (CH2Cl2, 293 K) ν(CO): 2035(s), 1865(m) cm−1.

4.3. Synthesis of [CAT]3[Co8Pd4C2(CO)24]. A solution obtained by adding NaOH (30 mg, 0.750 mmol) to

Figure 6. Molecular structures of (a) [Co8Pd4C2(CO)24]2− and (b) [Co8Pt4C2(CO)24]2− (orange, Pd; blue, Co; purple, disordered Pt; red, O; gray, C).

Figure 7. CoM4C2 cores of (a) [Co8Pd4C2(CO)24]2− and (b) [Co8Pt4C2(CO)24]2− (orange, Pd; blue, Co; purple, disordered Pt; Co; gray, C).

3. CONCLUSIONS

In summary, two structural isomers of the [HCo15Pd9C3(CO)38]2− nanoclusters have been isolated and their structures determined by single-crystal X-ray crystallography as several different salts and solvates. These nanoclusters are composed of a Pd9 core decorated on its surface by three Co6C(CO)12 organometallic units. The two isomers differ because of the different structures of the Pd9 core, which may be a tricapped octahedron (Oh-Pd9) or a tricapped trigonal prism (TP-Pd9). This represents a rare case of cluster core isomerism induced by weak crystal packing forces. Indeed, the presence in the solid state of the Oh-Pd9 or the TP-Pd9 isomer depends on the cation employed and/or the number and type of co-crystallized solvent molecules. Often, mixtures of the two isomers, within the same single crystal or as mixtures of different crystals within the same crystalization batch, are obtained. This is quite surprising, since weak intermolecular packing forces usually do not affect the total structure of nanoclusters, or their influence is limited to the surface ligands.

Cluster core isomerism has been recently documented also for Au−thiolates nanoclusters.21−25 A second type of structural isomerism found in Au−thiolate nanoclusters is staple isomerism, which is two clusters possessing the same metal core differ because of the disposition of the surface staple motives. A related surface ligand isomerism has been documented also for organometallic nanoclusters, and in particular in the case of cobalt and nickel carbide carbonyl clusters decorated on the surface by [AuPPh3]+ fragments.34,37,38

Despite the different nature of the metals and ligands involved in Au−thiolate and organometallic (carbonyl) molecular nanoclusters, there seems to be some general structural analogies among these categories of atomic precise nanoclusters.28,39,40 These analogies somehow regard the isomerization and dynamic behavior of their metal cores, as well as the protective and adaptive nature of the staple motives or ligand shells. As our understanding of the intimate total structures of metal nanoparticles is increasing, by watching them with the eye of molecular chemistry, concepts, which have been well consolidated along the years in coordination and organometallic chemistry, find their application also to describe metal nanoparticles.
radiation. Data corrections were performed with the program EXPO.

After washing with H2O (40 mL) and toluene (30 mL), the solution was treated with CH2Cl2. A mixture of PtCl2(Ph2P)2 (0.95 g, 2.13 mmol) and [NBu4]2[Co6C(CO)15] (3.10 mmol) was added to [NMe3(CH2Ph)]2[HCo15Pd9C3(CO)38] (0.41 g, 0.125 mmol) dissolved in CH2Cl2 (20 mL). After stirring at room temperature for 1 h, the mixture was filtered. A few crystals of [NMe3(CH2Ph)]2[HCo15Pd9C3(CO)38]·CH2Cl2 suitable for single-crystal X-ray studies were obtained by slow diffusion of n-hexane (40 mL) on the CH2Cl2 solution.

The asymmetric unit of the unit cell contains one cluster anion, two [NMe3(CH2Ph)]+ cations, and one CH2Cl2 molecule (all located on general positions). The cluster anion is disordered; since the occupancy factor of the main image is ca. 91%, it has been possible to locate only the Pd atoms of the minor image. The crystals are racemically twinned with refined Flack parameter 0.148(8). The C, O, and N atoms have been restrained to isotropic behavior (ISOR line in SHELXL, s.u. 0.001). Rigid bond restraints have been applied to the cluster anion (DELU line in SHELXL, s.u. 0.01). All aromatic rings have been constrained to fit regular hexagons (AFIX 66 line in SHELXL).

Similar U restraints have been applied to the [MePPh3]2[HCo15Pd9C3(CO)38]·CH2Cl2 molecule (SIMU line in SHELXL, s.u. 0.02). Rigid bond distances were applied as follows (s.u. 0.02): 1.75 Å for C–Cl in CH2Cl2.

4.6.3. [NBu4][HCo15Pd9C3(CO)38](100 K)(3)
The asymmetric unit of the unit cell contains one cluster anion, two [NEt3(CH2Ph)]+ cations, and one CH2Cl2 molecule (all located on general positions). The CH2Cl2 molecule is disordered and, therefore, its atoms have been split into two positions and refined isotropically using one occupancy parameter per disordered group. Some C and O atoms have been restrained to isotropic behavior (ISOR line in SHELXL, s.u. 0.01). Similar U restraints have been applied to the [NEt3(CH2Ph)]+ cations and CH2Cl2 molecule (SIMU line in SHELXL, s.u. 0.02). Rigid bond distances were applied as follows (s.u. 0.02): 1.75 Å for C–Cl in CH2Cl2.

4.6.4. [NEt3(CH2Ph)]2[HCo15Pd9C3(CO)38]·CH2Cl2 (293 K)(4)
The asymmetric unit of the unit cell contains one cluster anion, two [NEt3(CH2Ph)]+ cations, and one CH2Cl2 molecule (all located on general positions). The CH2Cl2 molecule is disordered and, therefore, its atoms have been split into two positions and refined isotropically using one occupancy parameter per disordered group. Some C and O atoms have been restrained to isotropic behavior (ISOR line in SHELXL, s.u. 0.01). Similar U restraints have been applied to the [NEt3(CH2Ph)]+ cations and CH2Cl2 molecule (SIMU line in SHELXL, s.u. 0.02). Rigid bond distances were applied as follows (s.u. 0.02): 1.75 Å for C–Cl in CH2Cl2.

4.6.5. [MePPh3]2[HCo15Pd9C3(CO)38]·2.5CH2Cl2 (100 K)(5)
The asymmetric unit of the unit cell contains one cluster anion, two [MePPh3]+ cations, and two CH2Cl2 molecules (all located on general positions), and half of a CH2Cl2 molecule equally disordered over two symmetry-related (by an inversion center) positions. Similar U restraints have been applied to the CH2Cl2 molecules (SIMU line in SHELXL, s.u. 0.01).

4.6.6. [MePPh3]2[HCo15Pd9C3(CO)38]·2.5CH2Cl2 (296 K)(6)
The asymmetric unit of the unit cell contains one cluster anion, two [MePPh3]+ cations, and two CH2Cl2 molecules (all located on general positions), and half of a CH2Cl2 molecule equally disordered over two symmetry-related (by an inversion center) positions. The cluster anion is disordered; since the occupancy factor of the main image is ca. 83%, it has been possible to locate only the Pd atoms of the minor image. Some C and O atoms have been restrained to isotropic behavior (ISOR line in SHELXL, s.u. 0.01). Similar U restraints have been applied to the [MePPh3]+ cations and CH2Cl2 molecules (SIMU line in SHELXL, s.u. 0.02). All aromatic rings have been constrained to fit regular hexagons (AFIX 66 line in SHELXL).

4.6.7. [MePPh3]2[HCo15Pd9C3(CO)38] (100 K)(7)
The asymmetric unit of the unit cell contains one-third of a cluster anion and one-third each of two [MePPh3]+ cations (all located on general positions).
The asymmetric unit of the unit cell contains one third of a cluster anion and one third of each of two \([\text{MePPh}_3\text{]+}\) cations (all located on 3-fold axes). The crystals are racemically twinned with refined Flack parameter 0.73(2).

4.6.8. \([\text{MePPh}_3\text{]+}]_2[\text{HCo}_5\text{Pd}_4\text{C}_2(\text{CO})_{18}]_\text{a} \) (293 K) (8). The asymmetric unit of the unit cell contains one third of a cluster anion and one third of each of two \([\text{MePPh}_3\text{]+}\) cations (all located on 3-fold axes). The crystals are racemically twinned with refined Flack parameter 0.68(4). Similar \(U\) restraints have been applied to the \([\text{MePPh}_3\text{]+}\) cations (SIMU line in SHELXL, s.u. 0.01). The \([\text{MePPh}_3\text{]+}\) cations have been restrained to isotropic behavior (ISOR line in SHELXL, s.u. 0.01).

4.6.9. \([\text{NMe}_3(\text{CH}_2\text{Ph})\text{]+}]_3[\text{Co}_{15}\text{Pd}_9\text{C}_3(\text{CO})_{38}]_\text{a}\cdot\text{CH}_2\text{Cl}_2 \) (Pt) (9). The asymmetric unit of the unit cell contains one cluster anion, three \([\text{NMe}_3(\text{CH}_2\text{Ph})\text{]+}\) cations, and one \text{CH}_2\text{Cl}_2 molecule (all located on general positions). One \([\text{NMe}_3(\text{CH}_2\text{Ph})\text{]+}\) cation is disordered and, therefore, its atoms have been split into two positions and refined using one occupancy parameter per disordered group. The C and O atoms of the CO ligands have been restrained to isotropic behavior (ISOR line in SHELXL, s.u. 0.005). Similar \(U\) restraints have been applied to the \([\text{NMe}_3(\text{CH}_2\text{Ph})\text{]+}\) cations (SIMU line in SHELXL, s.u. 0.02). The \([\text{NMe}_3(\text{CH}_2\text{Ph})\text{]+}\) cations have been restrained to have similar geometries (SAME line in SHELXL, s.u. 0.02). All aromatic rings have been constrained to fit regular hexagons (AFIX 66 line in SHELXL).

4.6.10. \([\text{NMe}_3(\text{CH}_2\text{Ph})\text{]+}]_3[\text{Co}_{15}\text{Pd}_9\text{C}_3(\text{CO})_{38}]_\text{a}\cdot\text{CH}_2\text{Cl}_2 \) (Pca2a) (10). The asymmetric unit of the unit cell contains one cluster anion, three \([\text{NMe}_3(\text{CH}_2\text{Ph})\text{]+}\) cations, and one \text{CH}_2\text{Cl}_2 molecule (all located on general positions). One \([\text{NMe}_3(\text{CH}_2\text{Ph})\text{]+}\) cation is disordered and, therefore, its atoms have been split into two positions and refined using one occupancy parameter per disordered group. The crystals are racemically twinned with refined Flack parameter 0.460(19). Some C and O atoms have been restrained to isotropic behavior (ISOR line in SHELXL, s.u. 0.001). The \([\text{NMe}_3(\text{CH}_2\text{Ph})\text{]+}\) cations have been restrained to have similar geometries (SAME line in SHELXL, s.u. 0.02). All aromatic rings have been constrained to fit regular hexagons (AFIX 66 line in SHELXL).

4.6.11. \([\text{MePPh}_3\text{]+}]_2[\text{Co}_{15}\text{Pd}_9\text{C}_3(\text{CO})_{38}]_\text{a}\cdot\text{CH}_2\text{Cl}_2 \) (11). The structure contains one independent cluster anion, three independent \([\text{MeNPh}_3\text{]+}\) cations, and one independent and disordered \text{CH}_2\text{Cl}_2 molecule (all located on general positions). The disordered \text{CH}_2\text{Cl}_2 molecule has been split into two positions and refined using one occupancy parameter per disordered group. Similar \(U\) restraints have been applied to the C and O atoms (SIMU line in SHELXL, s.u. 0.02). All aromatic rings have been constrained to fit regular hexagons (AFIX 66 line in SHELXL). Constraints to bond distances were applied as follows (s.u. 0.02): 1.75 Å for C−Cl in \text{CH}_2\text{Cl}_2.

4.6.12. \([\text{NMe}_3(\text{CH}_2\text{Ph})\text{]+}]_2[\text{Co}_{15}\text{Pd}_9\text{C}_3(\text{CO})_{38}]_\text{a}\cdot\text{CH}_2\text{Cl}_2 \) (12). The asymmetric unit of the unit cell contains two cluster anions, two \([\text{NMe}_3(\text{CH}_2\text{Ph})\text{]+}\) cations, and one \text{CH}_2\text{Cl}_2 molecule (all located on general positions).

4.6.13. \([\text{NBu}_4\text{]+}]_2[\text{Co}_{15}\text{Pd}_9\text{C}_3(\text{CO})_{38}]_\text{a} \) (13). The asymmetric unit of the unit cell contains half of a cluster anion (located on an inversion center) and one \([\text{NBu}_4\text{]+}\) cation (located on a general position). One \text{Bu} group of the \([\text{NBu}_4\text{]+}\) cation is disordered and, therefore, its atoms have been split into two positions and refined using one occupancy parameter per disordered group. Similar \(U\) restraints have been applied to the C and O atoms of the disordered groups (SIMU line in SHELXL, s.u. 0.01).

4.6.14. \([\text{NBu}_4\text{]+}]_2[\text{Co}_{8}\text{Pt}_4\text{C}_2(\text{CO})_{24}]_\text{a} \) (14). The asymmetric unit of the unit cell contains half of a cluster anion (located on an inversion center) and one \([\text{NBu}_4\text{]+}\) cation (located on a general position). \(M(1), M(2), \text{and} M(3)\) represent disordered positions, partially occupied by Co and Pt. A free variable was assigned to each position and dummy atom constraints (instructions EXYZ and EADP in SHELXL) adopted for their refinement. Similar \(U\) restraints have been applied to the \([\text{NBu}_4\text{]+}\) cation (SIMU line in SHELXL, s.u. 0.005). Restraints to bond distances were applied as follows (s.u. 0.01): 1.47 Å for C−N and 1.53 Å for C−C in \([\text{NBu}_4\text{]+}\).

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02109.

Crystallographic data (CIF)

Crystals and experimental details (PDF)

Accession Codes

CCDC 1862954–1862967 contain the supplementary crystallographic data for this article.

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Notes

The authors declare no competing financial interest.

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