Syntheses, structures and properties of primarily nanosized homo/heterometallic palladium CO/PR$_3$-ligated clusters

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Syntheses, properties and structures of nanosized palladium CO/PR$_3$-ligated homo- and heterometallic clusters containing up to 165 metal atoms are the focus of this review. The work discussed is primarily that of the authors and their coworkers. We propose that the unparalleled variety of structural types and the distinctive reactivities of neutral Pd$_n$(CO)$_x$(PR$_3$)$_y$ clusters composed of zerovalent Pd atoms are a consequence of relatively weak Pd–L(ligand) and Pd(0)–Pd(0) interactions that result from the stable 5s$^0$4d$^{10}$ closed-shell electron configuration of atomic Pd in its ground state.

Keywords: homo/heterometallic palladium clusters; synthesis; stereochemistry; X-ray crystallography

1. Introduction

There are two primary reasons for our long-standing interest in the chemistry of transition metal carbonyl clusters: the intriguing nature of their stereochemistry; bonding and reactivities that results from metal–metal and metal–ligand interactions; and their potential applications. The unpredictability of their structures (still the rule, rather than the exception) and the aesthetic beauty of the nanosized clusters, especially those that have highly symmetrical multi-shell frameworks, also make them appealing.

The initial synthetic route to the late transition metal carbonyl clusters usually involves the reduction of their salts, either with CO or with other reductants in the presence of CO. Although these procedures appear to be simple, the preparation of individual compounds often requires rigorously controlled reaction conditions. The compounds obtained in this way are normally of low-to-middle nuclearity (3 ≤ n ≤ 10) and can serve as precursors for reactions that give rise to high-nuclearity (nanosized) clusters. For metals of the Ni-triad, important starting compounds are [Ni$_6$(CO)$_{12}$]$^{2-}$, Pd$_{10}$(CO)$_{12}$(PR$_3$)$_6$, and [Pt$_{3n}$(CO)$_{6n}$]$^{2-}$. These further reactions involve thermolysis and electrostatically driven electrophile–nucleophile interactions, with the latter mainly pertaining to syntheses of

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heterometallic derivatives. In this review, we present the preparations, properties and molecular structures of primarily nanosized CO/PR$_3$-ligated homopalladium clusters, along with the stereochemistry of similarly ligated heterometallic Au−Pd, Ni−Pd and Pt−Pd clusters. Among transition metal carbonyls, these neutral Pd$_n$(CO)$_x$(PR$_3$)$_y$ clusters and their heterometallic derivatives are particularly remarkable in terms of their exceptional range in metal nuclearity (crystallographically varying from $n=3$ to 165) and the unusual diversity of their structural types. Since the last superb review (Femoni et al. 2006), indicating the possible contribution of high-nuclearity metal carbonyl clusters in nanoscience and nanotechnologies, the number of palladium clusters has considerably expanded to include the following new members that possess one or more interstitial metal atoms: Pd$_{37}$(CO)$_{28}$[P(p-Tolyl)$_3$]$_{12}$, Pd$_{52}$(CO)$_{36}$(PEt$_3$)$_{14}$, carbido Pd$_{36}$($\mu_4$-C)(CO)$_{28}$(PMe$_3$)$_{14}$, cationic [AuPd$_{22}$(CO)$_{20}$(PEt$_3$)$_8$]$^+$, anionic hydrido [HPd$_{30}$(CO)$_{26}$(PEt$_3$)$_{10}$]$^-$, Au$_4$Pd$_{28}$(CO)$_{26}$(PEt$_3$)$_{10}$, Au$_6$Pd$_{25}$(CO)$_{22}$(PMe$_3$)$_{16}$, Au$_4$Pd$_{32}$(CO)$_{28}$(PMe$_3$)$_{14}$ and ($\mu_{12}$-Pt)Pd$_{164}$−$x$Pt$_x$(CO)$_{72}$(PPh$_3$)$_{20}$ ($x \sim 7$).

(a) Syntheses of homopalladium Pd$_n$(CO)$_x$(PR$_3$)$_y$, $n \leq 10$, via reduction of Pd (II) precursors

Unlike nickel and platinum, palladium does not form discrete stable homoleptic carbonyl complexes/clusters in solution, and consequently, additional donor ligands such as phosphines are also required. The first reported trinuclear palladium clusters, ‘Pd$_3$(CO)$_3$(PPh$_3$)$_3$’ and Pd$_3$(CO)$_3$(PPh$_3$)$_4$, were prepared either by reduction of Pd(acac)$_2$ with AlEt$_3$ under CO or by reaction of PdCl$_2$(PPh$_3$)$_2$ with CO (Misono et al. 1969; Hidai et al. 1973). Later, a general method was developed that used Pd(OAc)$_2$ as the precursor and CO in a dual role of reductant/ligand, together with controlled amounts of phosphine in aqueous-organic solvents under adjusted acidity (Mednikov & Eremenko 1982 and references therein, 1983; Mednikov et al. 1984),

$$n\text{Pd(OAc)}_2 + (x + n)\text{CO} + y\text{PR}_3 + n\text{H}_2\text{O} \rightarrow \text{Pd}_n\text{(CO)}_x\text{(PR}_3)_y + n\text{CO}_2 + 2n\text{HOAc},$$

(1.1)

This method is applicable for a variety of PR$_3$ ligands (for example, R=Alk= C$_2$H$_5$, n-C$_3$H$_9$, n-C$_8$H$_{17}$, n-C$_{12}$H$_{25}$; R=Ar=C$_6$H$_5$, C$_6$H$_4$-$p$-CH$_3$, C$_6$H$_4$-$p$-OCH$_3$) in affording two types of interconvertible Pd$_4$ and Pd$_{10}$ clusters. Trinuclear clusters, such as Pd$_3$(CO)$_3$L$_4$ (L=PAr$_3$), were also obtained, as well as the earlier reported ‘Pd$_3$(CO)$_3$(PPh$_3$)$_3$’, whose composition was crystallographically reformulated as a butterfly Pd$_4$(CO)$_5$L$_4$ (L=PPh$_3$); an analogue of the latter with L=PPh$_2$Me was also obtained by reduction of Pd(NO$_2$)$_2$L$_2$ with CO in CH$_2$Cl$_2$ (Dubraski et al. 1980). The most important outcome of reaction (1.1) is the formation of new Pd$_{10}$ clusters in high yields (up to 80–90%). X-ray crystal structures of those with L=PBU$_n$$_3$, namely, Pd$_{10}$(CO)$_{12}$PBU$_n$$_3$$_6$ and Pd$_{10}$(CO)$_{14}$(PBU$_n$$_3$)$_4$, were determined by Slovokhotov and Struchkov (Mednikov et al. 1981, 1983). Both structures consist of Pd$_6$ octahedra with four additional tetrahedrally linked open-capped Pd atoms (figure 1). Its structural analogue, Pd$_{10}$(CO)$_{12}$L$_6$, (L=PEt$_3$), was also obtained in good yield (73%) from the reaction of Pd$_2$dba$_3$ (dba=dibenzylideneacetone) with CO and PEt$_3$.
Figure 1. Molecular structure of Pd_{10}(CO)_{12}(PBu_3)_6 with four wingtip (open-capped) Pd atoms upon non-adjacent faces of the Pd_6 octahedron. In Pd_{10}(CO)_{14}(PBu_3)_4, two terminal CO’s are attached to apical Pd atoms instead of two PBu_3 ligands. CO ligands are in wire. (Mingos & Hill 1995). Other neutral representatives of this family, all with L = PMe_3, are Pd_6(CO)_4L_7 (Klein & Mager 1992), Pd_7(CO)_7L_7 (Goddard et al. 1982) and Pd_8(CO)_8L_7 (Bochmann et al. 1987).

2. Towards nanosized homopalladium clusters

(a) Conversions within the Pd_n(CO)_x(PR_3)_y family

Investigations of the reactivities of the Pd_{10}(CO)_{12}L_6 clusters have given rise to the wide variety of nanosized clusters with Pd_n nuclearities of n = 12–145. The relatively low cohesive energy of Pd (377 kJ mol\(^{-1}\)) and the relatively weak coordination of CO and PR_3 ligands to Pd(0) (in contrast to that of zerovalent Ni and Pt) greatly facilitate cluster growth. In fact, Pd_n(CO)_x(PR_3)_y with n = 4, 10 are stable only under a CO atmosphere. The replacement of CO over solutions of Pd_{10}(CO)_{12}L_6 with an inert gas (e.g. N_2, Ar) triggers its spontaneous conversion into Pd_{23}(CO)_{20}L_{10} for L=PEt_3 (yield, 15%) and PMe_2Ph (approx. 7%) (Mednikov et al. 2005a). The structure of the Pd_{23} cluster (L=PEt_3) (figure 2) is discussed later in this article. Thermolysis reactions, either with or without the use of reagents that bind CO/PR_3 ligands, significantly increase the yields of Pd_{23}(CO)_{20}L_{10}, L=PEt_3, PBu_3^n, PMe_2Ph. A series of Pd_n clusters (12 \leq n \leq 145) were prepared in this way. Cluster growth is affected by a number of factors, if not all possible ones, such as the composition of the precursor, the type and concentration of the deligation reagent, the duration of the reaction, the dynamics in the removal of liberating CO, the temperature and the solvent. Nevertheless, a number of sufficiently selective pathways have been uncovered (table 1).
Deligation reactions from Pd(0) include the following:

(a) acid/base

$$\text{PR}_3 + \text{HX} \rightarrow [\text{HPR}_3]^+ \text{X}^-, \quad \text{X}^- = \text{CH}_3\text{CO}_2^-, \text{HCO}_2^-, \text{CF}_3\text{CO}_2^-,$$

$$\text{CO} + \text{OH}^- \rightarrow \text{HCO}_2^-,$$  \hspace{1cm} (2.1)

(b) oxidation

$$\text{CO} + [\text{O}] \rightarrow \text{CO}_2,$$

$$\text{PR}_3 + [\text{O}] \rightarrow \text{OPR}_3, \quad [\text{O}] = \text{Me}_3\text{NO}, \text{O}_2, \text{H}_2\text{O}_2,$$  \hspace{1cm} (2.3)

and

(c) complexation

$$\text{PR}_3 + \text{Pd(OAc)}_2 \rightarrow \frac{1}{2} (\text{PR}_3)_2\text{Pd}_2(\text{OAc})_4 \ldots,$$

$$\text{PR}_3 + \text{M}_x(\text{CO})_y \rightarrow \text{M}_x(\text{CO})_{y-1}(\text{PR}_3) + \text{CO}, \quad \text{M} = \text{Fe}, \text{Co}, \text{Ni}.$$  \hspace{1cm} (2.5)

Controlled cluster growth may be achieved via (i) combined application of reactions (a) and (b), (ii) changes in the concentrations of deligating reagents, and (iii) variation in the nuclearities of the Pd$_n$ precursor, Pd$_4$ or Pd$_{10}$. Complementary pathways involve generation of reactive ‘naked’ (highly coordinatively unsaturated) [Pd] species \textit{in situ} (equations (2.7) and (2.8)) that,
Table 1. Conditions of syntheses of Pd\(_n\)(CO)\(_x\)(PAk\(_3\))\(_y\) clusters, \(n \geq 12\), under inert atmosphere (Ar or N\(_2\)). DMF is dimethylformamide, THF is tetrahydrofuran.\(^a\)

<table>
<thead>
<tr>
<th>entry</th>
<th>precursor</th>
<th>deligation reagent(s), ratio to precursor, temperature, CO removal(^b)</th>
<th>solvent</th>
<th>product</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(<em>{10})(CO)(</em>{12})(PBU(_3))(_6)</td>
<td>Pd(<em>{10})/Pd(</em>{2})dba(_3) = 1/1</td>
<td>Me(_2)CO/EtOH</td>
<td>Pd(<em>{12})(CO)(</em>{12})(PBU(_3))(_6)</td>
<td>41, based on Pd(_{10})</td>
</tr>
<tr>
<td>2</td>
<td>Pd(_{4})(CO)(_5)(PET(_3))(_4)</td>
<td>Pd(_{4})/Me(_3)NO = 1/5, 2 h</td>
<td>Me(_2)CO/Et(_2)O/EtOH/HOAc</td>
<td>Pd(<em>{16})(CO)(</em>{13})(PET(_3))(_9)</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>Pd(<em>{10})(CO)(</em>{12})(PET(_3))(_6)</td>
<td>Pd(_{10})/Me(_3)NO = 1/2, 3 h, 24 h</td>
<td>Me(_2)CO/Et(_2)O/EtOH/25% Me(_3)N</td>
<td>Pd(<em>{16})(CO)(</em>{13})(PET(_3))(_9)</td>
<td>74</td>
</tr>
<tr>
<td>4</td>
<td>Pd(_{4})(CO)(_5)(PET(_3))(_4)</td>
<td>Pd(_{4})/Pd(OAc)(_2) = 1/1.1</td>
<td>Me(_2)CO/EtO</td>
<td>Pd(<em>{23})(CO)(</em>{20})(PET(_3))(_10)</td>
<td>81</td>
</tr>
<tr>
<td>5</td>
<td>Pd(<em>{10})(CO)(</em>{12})(PET(_3))(_6)</td>
<td>Pd(_{10})/Me(_3)NO/HOAc = 1/4/4</td>
<td>Me(_2)CO/Et(_2)O/EtOH</td>
<td>Pd(<em>{23})(CO)(</em>{20})(PET(_3))(_10)</td>
<td>73</td>
</tr>
<tr>
<td>6</td>
<td>Pd(<em>{10})(CO)(</em>{12})(PET(_3))(_6)</td>
<td>50(^\circ)C, 10 min, 90 min</td>
<td>Me(_2)CO/HOAc</td>
<td>Pd(<em>{23})(CO)(</em>{20})(PET(_3))(_8)</td>
<td>71</td>
</tr>
<tr>
<td>7</td>
<td>Pd(<em>{10})(CO)(</em>{12})(PET(_3))(_6)</td>
<td>Pd(_{10})/Ni(1.5-COD)(_2) = 1/2.5</td>
<td>Me(_2)CO/i-Pr(_2)O</td>
<td>Pd(<em>{23})(CO)(</em>{20})(PET(_3))(_8)</td>
<td>79</td>
</tr>
<tr>
<td>8</td>
<td>Pd(<em>{12})(CO)(</em>{12})(PBU(_3))(_6)</td>
<td>Pd(_{12})/Pd(OAc)(_2) = 1/1.4, 50(^\circ)C</td>
<td>toluene, then MeOH/MeCN</td>
<td>Pd(<em>{23})(CO)(</em>{20})(PBU(_3))(_10)</td>
<td>78</td>
</tr>
<tr>
<td>9</td>
<td>Pd(<em>{10})(CO)(</em>{12})(PBU(_3))(_6)</td>
<td>50(^\circ)C, 2 h</td>
<td>Et(_2)O/Me(_2)CO/HOAc/H(_2)O</td>
<td>Pd(<em>{23})(CO)(</em>{20})(PBU(_3))(_10)</td>
<td>59</td>
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<tr>
<td>10</td>
<td>Pd(<em>{10})(CO)(</em>{12})(PET(_3))(_6)</td>
<td>Pd(_{10})/HCO(_2)H = 1/200</td>
<td>Me(_2)CO/THF</td>
<td>Pd(<em>{23})(CO)(</em>{20})(PET(_3))(_8)</td>
<td>57</td>
</tr>
<tr>
<td>11</td>
<td>Pd(<em>{10})(CO)(</em>{12})(PET(_3))(_6)</td>
<td>Pd(_{10})/Me(_3)NO = 1/4, 50(^\circ)C, 15 min, 60 min</td>
<td>Me(_2)CO/EtOH/HOAc</td>
<td>Pd(<em>{23})(CO)(</em>{20})(PET(_3))(_8)</td>
<td>54</td>
</tr>
<tr>
<td>12</td>
<td>Pd(<em>{10})(CO)(</em>{12})(PET(_3))(_6)</td>
<td>Pd(_{10})/CF(_3)CO(_2)H = 1/20(^c)</td>
<td>Me(_2)CO/i-Pr(_2)O</td>
<td>Pd(<em>{30})(CO)(</em>{26})(PET(_3))(_10)</td>
<td>low, &lt;5</td>
</tr>
<tr>
<td>13</td>
<td>Pd(<em>{10})(CO)(</em>{12})(PET(_3))(_6)</td>
<td>Pd(<em>{10})/Pd(</em>{2})dba(_3) = 1/2.5</td>
<td>Me(_2)CO/Et(_2)O</td>
<td>Pd(<em>{31})(CO)(</em>{24})(PET(_3))(_12)</td>
<td>119(^d)</td>
</tr>
<tr>
<td>14</td>
<td>Pd(<em>{10})(CO)(</em>{12}) (PET(_3))(_6)</td>
<td>65(^\circ)C</td>
<td>THF</td>
<td>Pd(<em>{37})(CO)(</em>{28})({P(p-Tolyl)})(<em>3)(</em>{12}</td>
<td>56</td>
</tr>
<tr>
<td>15</td>
<td>Pd(<em>{10})(CO)(</em>{12})(PET(_3))(_6)</td>
<td>Pd(_{10})/Me(_3)NO/CF(_3)CO(_2)H = 1/4/30</td>
<td>Me(_2)CO/Et(_2)O</td>
<td>Pd(<em>{38})(CO)(</em>{28})(PET(_3))(_12)</td>
<td>60</td>
</tr>
<tr>
<td>16</td>
<td>Pd(<em>{10})(CO)(</em>{12})(PET(_3))(_6)</td>
<td>Pd(<em>{10}/Pd(</em>{2})dba(_3) = 1/3.5, 50(^\circ)C</td>
<td>Me(_2)CO/i-Pr(_2)O, then H(_2)O</td>
<td>Pd(<em>{52})(CO)(</em>{30})(PET(_3))(_14)</td>
<td>low, &lt;5</td>
</tr>
<tr>
<td>17</td>
<td>Pd(<em>{10})(CO)(</em>{12})(PET(_3))(_6)</td>
<td>Pd(_{10})/HCO(_2)H = 1/70</td>
<td>Me(_2)CO/Et(_2)O</td>
<td>Pd(<em>{51})(CO)(</em>{40})(PET(_3))(_14)</td>
<td>low, &lt;1</td>
</tr>
<tr>
<td>18</td>
<td>Pd(<em>{10})(CO)(</em>{12})(PET(_3))(_6)</td>
<td>Pd(_{10}/[Pd(Me(_2)CN)(_2)H(_2)]^{1+} = 1/2</td>
<td>THF/Me(_2)CO, then MeCN</td>
<td>Pd(<em>{66})(CO)(</em>{45})(PET(_3))(_16)</td>
<td>13</td>
</tr>
<tr>
<td>19</td>
<td>Pd(<em>{10})(CO)(</em>{12})(PET(_3))(_6)</td>
<td>Pd(_{10}/Me(_3)NO/CF(_3)CO(_2)H = 1/16/120</td>
<td>Me(_2)CO/THF/i-Pr(_2)O or Et(_2)O</td>
<td>Pd(<em>{66})(CO)(</em>{25})(PET(_3))(_10), x \sim 46</td>
<td>45–50</td>
</tr>
<tr>
<td>20</td>
<td>Pd(<em>{10})(CO)(</em>{12})(PET(_3))(_6)</td>
<td>Pd(_{10}/Me(_3)NO = 1/8; NaOH, 50(^\circ)C</td>
<td>DMF, then MeCN</td>
<td>Pd(<em>{69})(CO)(</em>{36})(PET(_3))(_18)</td>
<td>50</td>
</tr>
<tr>
<td>21</td>
<td>Pd(PET(_3))(_2)Cl(_2)+ Au(PH(_3))Cl(_6)</td>
<td>NaOH, 2 days CO, then N(_2)</td>
<td>DMF, then MeOH</td>
<td>Pd(<em>{145})(CO)(</em>{12})(PET(_3))(_30), x \sim 60</td>
<td>low</td>
</tr>
</tbody>
</table>

\(^a\)Data are taken from work of authors and coworkers.
\(^b\)Time from the beginning of the reaction to the short-time renewal of the atmosphere with an inert gas.
\(^c\)1 h stirring under N\(_2\), 2 h under CO, then N\(_2\).
\(^d\)Based on Pd\(_{10}\) that clearly indicates on incorporation of Pd(0) atoms from Pd\(_{2}\)dba\(_3\) into final Pd\(_{34}\).
\(^e\)Later, the Pd\(_{145}\) was obtained with higher yield from Pd\(_{10}\) (Tran & Dahl 2003).
in the presence, for example, of Pd₄ or Pd₁₀ precursors, result in a consecutive aggregation (equation (2.9)),

\[
Pd(OAc)₂ + HCO₂H \rightarrow [Pd] \rightarrow CO₂, H₂O, \text{reductants} \quad \text{(2.7)}
\]

\[
Pd₂dba₃ \rightarrow [Pd], \quad \text{dba = dibenzylideneacetone,} \quad \text{(2.8)}
\]

and \( Pd₄ \) or \( Pd₁ₐ + [Pd] \rightarrow Pdₙ(CO)ₓ(PR₃)ᵧ, \quad n > 10. \quad \text{(2.9)}

Widely applied solvents for syntheses of PEt₃-derivatives were mixtures of acetone with Et₂O, \( i-Pr₂O \), or tetrahydrofuran (THF) in ratios of approximately 3/1 that dissolved the starting \( Pd₁₀ \) but not the \( Pdₙ>₁₀ \) products, and thereby directly afforded crystalline materials.

\( (b) \) Syntheses from anionic Pd/Ni precursors

An unexpectedly valuable precursor for the synthesis of \( Pdₙ(CO)ₓLᵧ \) clusters, in particular those with \( L=\text{PMe₃} \), has proven to be the bimetallic carbonyl-ligated Pd/Ni cluster, \( [Pd₁₃Ni₁₃(CO)₃₄]⁻ \) (as \( [\text{PPh₄}]⁺ \) salt), that was prepared in high yields (more than 90%) from reactions of either \( Pd(OAc)₂ \) or \( Pd(MeCN)₄(BF₄)₂ \) with \( [\text{Ni₆(CO)}₁₂]⁻ \) (Tran et al. 2000). Its reactions with \( \text{PMe₃} \) mainly in the presence of HOAc gave rise to four homometallic icosahedral-based clusters consisting of \( Pd₁₆(CO)₁₃(\text{PMe₃})₉ \) (16–52%), \( Pd₃₅(CO)₂₃(\text{PMe₃})₁₅ \) (15%), \( Pd₃₉(CO)₂₃(\text{PMe₃})₁₆ \) (27–50%) and \( Pd₅₉(CO)₃₂(\text{PMe₃})₂₁ \) (40%). These clusters were separated by consecutive extractions with different solvents followed by appropriate crystallizations (Tran et al. 1998, 2001). Later, all four were obtained from \( Pd₁₀(CO)₁₂(\text{PMe₃})₆ \) by CO/PMe₃-deligation reactions (E. G. Mednikov & L. F. Dahl 2002, unpublished data). The \( [Pd₁₃Ni₁₃(CO)₃₄]⁻ \) anion was subsequently used for the synthesis of \( Pd₁₆(CO)₁₃(\text{PEt₃})₉, Pd₂₃(CO)₂₀(\text{PEt₃})₁₀, Pd₂₃(CO)₂₀(\text{PPr₃})₈, Pd₃₄(CO)₂₄(\text{PEt₃})₁₂ \) and the heterometallic \( Pd₉Ni₉(CO)₁₇(\text{PEt₃})₉ \) (Wittayakun 2000).

3. Spectroscopic characterizations

Infrared spectroscopy was found to be a convenient, reliable method for identification of many \( Pdₙ(CO)ₓ(PR₃)ᵧ \) clusters, \( n < 40, \) for which X-ray crystal structures have been obtained. In contrast to Ni and Pt carbonyl clusters that conventionally possess terminal CO ligands, all CO/PR₃-ligated homopalladium clusters, with the exception of \( Pd₁₀(CO)₂(\mu₂-CO)₈(\mu₃-CO)₄(PBu₃)₄ \) and its analogues, have only doubly and triply bridging CO’s with observed stretching vibrations in the range of 1920–1650 cm⁻¹ (table 2). Apparently, this is primarily the consequence of relatively weak zerovalent Pd–Pd interactions that require stabilization by bridging carbonyl ligands. Clusters with unmistakable IR-fingerprinting characteristics are: \( Pd₁₀(CO)₁₂(PR₃)₆, Pd₁₀(CO)₁₄(PBu₃)₁₄; Pd₁₂(CO)₁₂(PBu₃)₆; Pd₁₆(CO)₁₃L₉ \) with \( L=\text{PMe₃, PEt₃, PPr₃, PPr₃} ; Pd₂₃(CO)₂₀(PEt₃)₈; Pd₃₄(CO)₂₄(PEt₃)₁₂; \) and \( Pd₃₈(CO)₂₅L₁₂ \) with \( L=\text{PEt₃, PBu₃} \). Identification by IR spectroscopy of \( Pdₙ \) clusters with \( n > 50 \) is greatly hindered by the pseudo-simplicity of the spectra, which usually have one band (often broad), with or without shoulders, as illustrated by entries 18–23 in table 2.
Table 2. IR spectra of \( \text{Pd}_n(\text{CO})_x(\text{PR}_3)_y \) clusters, \( n \geq 10 \).\(^a\)

<table>
<thead>
<tr>
<th>entry</th>
<th>cluster</th>
<th>( \nu(\text{CO}), \text{cm}^{-1} ) (in Nujol, if otherwise stated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{Pd}<em>{10}(\text{CO})</em>{12}(\text{PEt}_3)_6 )</td>
<td>1889 s, 1850 s, 1791 m; 1893 s, 1877 w-m, 1854 s, 1793 w (in CHCl(_3))</td>
</tr>
<tr>
<td>2</td>
<td>( \text{Pd}<em>{10}(\text{CO})</em>{12}(\text{PBu}_3)_6 )</td>
<td>1884 s, 1850 s, 1799 m; 1892 s, 1874 w-m, 1857 s (in CHCl(_3))</td>
</tr>
<tr>
<td>3</td>
<td>( \text{Pd}<em>{10}(\text{CO})</em>{14}(\text{PBu}_3)_4 )</td>
<td>2033 s, 1913 s, 1870 s, 1818 s; 2035 s, 1915 s, 1898 sh, 1875 s (in toluene); 2042 s, 1915 s, 1901 sh, 1875 s (in CHCl(_3))</td>
</tr>
<tr>
<td>4</td>
<td>( \text{Pd}<em>{12}(\text{CO})</em>{12}(\text{PBu}_3)_6 )</td>
<td>1881 m, 1859 s, 1803 s</td>
</tr>
<tr>
<td>5</td>
<td>( \text{Pd}<em>{16}(\text{CO})</em>{13}(\text{PEt}_3)_9 )</td>
<td>1869–1868 s, 1837–1834 s, 1760–1756 sh, 1738–1735 m, 1713–1710 m-w or w, 1667–1666 m-w or w; 1865 s, 1833 s, 1740 s-m, 1720–1698 sh w (in CHCl(_3), Ar); 2038 w-m, 2020 w-m, 1891 s, 1875 s, 1857 s-m, 1793 sh w, 1602 w-m (in CHCl(_3), under CO)</td>
</tr>
<tr>
<td>6</td>
<td>( \text{Pd}<em>{16}(\text{CO})</em>{13}(\text{PMc}_3)_9 )</td>
<td>1870 vs, 1835 vs, 1762 w(sh), 1747 m, 1725 w, 1668 m (in THF)</td>
</tr>
<tr>
<td>7</td>
<td>( \text{Pd}<em>{23}(\text{CO})</em>{20}(\text{PEt}_3)_8 )</td>
<td>1872 s, 1842 s-m, 1818 s-m</td>
</tr>
<tr>
<td>8</td>
<td>( \text{Pd}<em>{23}(\text{CO})</em>{20}(\text{PBu}_3)_8 )</td>
<td>1877 s, 1844 m, 1824 m</td>
</tr>
<tr>
<td>9</td>
<td>( \text{Pd}<em>{23}(\text{CO})</em>{20}(\text{PEt}<em>3)</em>{10} )</td>
<td>1870–1867 (vs-s), 1855–1853 (sh), 1838 (w/sh), 1830–1829 (w/sh), 1824–1822 (m/sh or mw/sh), 1785–1784 (w-vw), 1756–1754 (vw); 1868 s, 1839 sh, 1820 m (in THF)</td>
</tr>
<tr>
<td>10</td>
<td>( \text{Pd}<em>{23}(\text{CO})</em>{21}(\text{PEt}<em>3)</em>{10} )</td>
<td>1869 s, 1854 sh, 1830 m-w, 1825 m-w</td>
</tr>
<tr>
<td>11</td>
<td>( \text{Pd}<em>{23}(\text{CO})</em>{22}(\text{PEt}<em>3)</em>{10} )</td>
<td>1863 s, 1847 sh, 1823 sh</td>
</tr>
<tr>
<td>12</td>
<td>( \text{Pd}<em>{23}(\text{CO})</em>{20}(\text{PBu}<em>3)</em>{10} )</td>
<td>1870 s, 1857 sh, 1833 m, 1791 w</td>
</tr>
<tr>
<td>13</td>
<td>( \text{Pd}<em>{30}(\text{CO})</em>{26}(\text{PEt}<em>3)</em>{10} )</td>
<td>1910 m, 1881 s, 1864 sh</td>
</tr>
<tr>
<td>14</td>
<td>( \text{Pd}<em>{34}(\text{CO})</em>{24}(\text{PEt}<em>3)</em>{12} )</td>
<td>1893 s, 1866 s, 1837 s, 1809 s; averaged: 1893–1890 s, 1866–1864 s, 1838–1836 s, 1809–1808 s or s-m</td>
</tr>
<tr>
<td>15</td>
<td>( \text{Pd}<em>{37}(\text{CO})</em>{28}[(\rho-\text{Tol})<em>3]</em>{12} )</td>
<td>1895 s, 1868 sh, 1852 m</td>
</tr>
<tr>
<td>16</td>
<td>( \text{Pd}<em>{38}(\text{CO})</em>{28}(\text{PEt}<em>3)</em>{12} )</td>
<td>1899 s, 1885 s-m, 1850 s, 1840 s-m, 1817 w</td>
</tr>
<tr>
<td>17</td>
<td>( \text{Pd}<em>{38}(\text{CO})</em>{28}(\text{PBu}<em>3)</em>{12} )</td>
<td>1902 m, 1889 sh, 1852 m, 1845 sh, 1816 w</td>
</tr>
<tr>
<td>18</td>
<td>( \text{Pd}<em>{52}(\text{CO})</em>{36}(\text{PEt}<em>3)</em>{14} )</td>
<td>1875 sh, 1869 sh, 1856 s</td>
</tr>
<tr>
<td>19</td>
<td>( \text{Pd}<em>{54}(\text{CO})</em>{40}(\text{PEt}<em>3)</em>{14} )</td>
<td>1920 m-w, 1878–1877 s, 1802 w</td>
</tr>
<tr>
<td>20</td>
<td>( \text{Pd}<em>{66}(\text{CO})</em>{45}(\text{PEt}<em>3)</em>{16} )</td>
<td>1916 sh, 1884 s br, 1867 sh</td>
</tr>
<tr>
<td>21</td>
<td>( \text{Pd}_{66}(\text{CO})_x(\text{PEt}<em>3)</em>{16}, x \sim 46 )</td>
<td>1883–1881 s br</td>
</tr>
<tr>
<td>22</td>
<td>( \text{Pd}<em>{69}(\text{CO})</em>{36}(\text{PEt}<em>3)</em>{18} )</td>
<td>1855 s, 1830 sh, 1869 s, 1826 sh (in THF)</td>
</tr>
<tr>
<td>23</td>
<td>( \text{Pd}_{145}(\text{CO})_x(\text{PEt}<em>3)</em>{30}, x \sim 60 )</td>
<td>1870 s (in THF)</td>
</tr>
</tbody>
</table>

\(^a\)Data are taken from work of authors and coworkers.

Nuclear magnetic resonance (NMR) spectroscopic studies of \( \text{Pd}_n \) clusters in solution have been carried out mainly on \( ^{31}\text{P} \) nuclei, because of both accessibility and informativeness. These data can be roughly classified into two groups: those with solution spectra matching the corresponding solid-state structures (table 3, entries 1–9), and those that do not (table 3, entries 10–11). Owing to the low solubilities or small yields of \( \text{Pd}_n > 60 \) clusters, as well as what we assume may involve ligand migration, their NMR spectra are either unavailable or non-interpretable in a clear-cut way.

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Table 3. $^{31}$P$^1$H NMR spectra of Pd$_n$(CO)$_x$(PR$_3$)$_y$ clusters, $n \geq 10$.\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>entry</th>
<th>compound</th>
<th>chemical shifts, ppm (multiplicity); splitting constants</th>
<th>intensity ratios</th>
<th>solvent, atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd$<em>{10}$(CO)$</em>{12}$(PEt$_3$)$_6$</td>
<td>$\delta_1 = 11.4$ (d, $^3J_{P-P} = 4.2$ Hz), $\delta_2 = 3.5$ (t, insufficiently resolved)</td>
<td>$\delta_1/\delta_2 = 2/1$</td>
<td>C$_6$D$_6$, CO</td>
</tr>
<tr>
<td>2</td>
<td>Pd$<em>{12}$(CO)$</em>{12}$(PBA$_3^3$)$_6$</td>
<td>$\delta_1 = -3.4$ (s)</td>
<td></td>
<td>toluene-d$_8$, N$_2$</td>
</tr>
<tr>
<td>3</td>
<td>Pd$<em>{16}$(CO)$</em>{13}$(PEt$_3$)$_9$</td>
<td>$\delta_1 = 18.24$ (d, 3P, $^1J_{P-P} = 31.3$ Hz), $\delta_2 = -0.71$ (d, 3P, $^1J_{P-P} = 31.7$ Hz), $\delta_3 = -1.03$ (s, 3P)</td>
<td>$\delta_1/\delta_2/\delta_3 = 1/1/1$</td>
<td>C$_6$D$_6$, N$_2$</td>
</tr>
<tr>
<td>4</td>
<td>Pd$<em>{16}$(CO)$</em>{13}$(PMe$_3$)$_9$</td>
<td>$\delta_1 = -12.22$ (s, 3P), $\delta_2 = -13.18$ (d, 3P, $^1J_{P-P} = 84.0$ Hz), $\delta_3 = -24.28$ (d, 3P, $^1J_{P-P} = 80.0$ Hz)</td>
<td>$\delta_1/\delta_2/\delta_3 = 1/1/1$</td>
<td>acetone-d$_6$, N$_2$</td>
</tr>
<tr>
<td>5</td>
<td>Pd$<em>{24}$(CO)$</em>{20}$(PEt$_3$)$_8$</td>
<td>$\delta_1 = 13.9$ (s), $\delta_2 = 9.6$ (s)</td>
<td>$\delta_1/\delta_2 = 1/1$</td>
<td>C$_6$D$_6$, N$_2$</td>
</tr>
<tr>
<td>6</td>
<td>Pd$<em>{23}$(CO)$</em>{20}$(PMe$_3$)$_9$</td>
<td>$\delta_1 = 6.2$ (s), $\delta_2 = 4.8$ (t), $^1J_{P-P} = 3.6$ Hz, $\delta_3 = 3.3$ (s); $\delta_1 = 10.2$ (s), $\delta_2 = 9.0$ (s), $\delta_3 = 7.7$ (s)</td>
<td>$\delta_1/\delta_2/\delta_3 = 2/4/4$; $\delta_1/\delta_2/\delta_3 = 2/4/4$</td>
<td>C$_6$D$_6$, N$_2$; THF-d$_8$, N$_2$</td>
</tr>
<tr>
<td>7</td>
<td>Pd$<em>{12}$(CO)$</em>{20}$(PBA$_3^3$)$_10$</td>
<td>$\delta_1 = -2.0$ (s), $\delta_2 = -4.5$ (t), $^1J_{P-P} = 4.2$ Hz, $\delta_3 = -6.4$ (s)</td>
<td>$\delta_1/\delta_2/\delta_3 = 2/4/4$</td>
<td>C$_6$D$_6$, N$_2$</td>
</tr>
<tr>
<td>8</td>
<td>Pd$<em>{34}$(CO)$</em>{24}$(PEt$<em>3$)$</em>{12}$</td>
<td>$\delta_1 = 12.9$ (d, $^1J_{P-P} = 9.7$ Hz), $\delta_2 = 9.2$ (s), $\delta_3 = -5.5$ (d, $^1J_{P-P} = 12.3$ Hz)</td>
<td>$\delta_1/\delta_2/\delta_3 = 4/4/4$</td>
<td>C$_6$D$_6$, N$_2$</td>
</tr>
<tr>
<td>9</td>
<td>Pd$<em>{35}$(CO)$</em>{25}$(PMe$<em>3$)$</em>{15}$</td>
<td>$\delta_1 = 31.3$ (s), $\delta_2 = -24.4$ (s), $\delta_3 = -25.0$ (d, $^1J_{P-P} = 29.0$ Hz), $\delta_4 = -37.1$ (d, $^1J_{P-P} = 33.0$ Hz)</td>
<td>$\delta_1/\delta_2/\delta_3/\delta_4 = 1/1/1$</td>
<td>THF-d$_8$, N$_2$</td>
</tr>
<tr>
<td>10</td>
<td>Pd$<em>{37}$(CO)$</em>{28}$(P(p-Tolyl)$<em>3$)$</em>{12}$</td>
<td>$\delta_1 = 41.5$ (s br), $\delta_2 = 28.5$ (s br), $\delta_3 = 27.4$ (s), $\delta_4 = 25.3$ (s br), $\delta_5 = 20.2$ (s br), $^1J_{P-P} = 33.0$ Hz)</td>
<td>$\delta_1/\delta_2/\delta_3/\delta_4/\delta_5 \approx 1.0/0.9/1.5/1.5/1.7$</td>
<td>CD$_2$Cl$_2$, N$_2$</td>
</tr>
<tr>
<td>11</td>
<td>Pd$<em>{39}$(CO)$</em>{23}$(PMe$<em>3$)$</em>{16}$</td>
<td>$\delta_1 = 30.92$ (s)</td>
<td></td>
<td>THF-d$_8$, N$_2$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Room temperature, reference 85% H$_3$PO$_4$ in D$_2$O, external.

\textsuperscript{b}Data are taken from work of authors and coworkers.
4. Electrochemical properties

In general, Pd$_n$(CO)$_x$(PR$_3$)$_y$ clusters in solution are either not sufficiently soluble or not stable for an appreciable time (vide supra). Thus, electrochemical studies were limited. Cyclic voltammetric (CV) measurements of solutions of Pd$_{23}$(CO)$_{20}$(PEt$_3$)$_{10}$ (denoted as Pd$_{23}$P$_{10}$) in THF showed one quasi-reversible two-electron reduction [Pd$_{23}$P$_{10}$]/[Pd$_{23}$P$_{10}$]$^{2-}$ ($E_{1/2}$ = −0.91 V) and two quasi-reversible one-electron oxidations [Pd$_{23}$P$_{10}$]/[Pd$_{23}$P$_{10}$]$^{1+}$ and [Pd$_{23}$P$_{10}$]$^{1+}$/[Pd$_{23}$P$_{10}$]$^{2+}$ at $E_{1/2}$ = 0.08 and 0.32 V, respectively (versus Ag/AgCl; Mednikov et al. 2005a). After several cycles, the formation of Pd$_{23}$(CO)$_{20}$(PEt$_3$)$_{8}$ (denoted as Pd$_{23}$P$_{8}$) was detected. The Pd$_{23}$P$_{8}$ cluster, which has two less phosphine ligands than its precursor, has a totally different structure, namely a highly deformed body-centred cubic geometry rather than the face-centred cubic (v$_2$-octahedral) geometry of Pd$_{23}$P$_{10}$ (Mednikov et al. 1987b). Its CV displayed a reversible two-electron reduction of Pd$_{23}$P$_{8}$/[Pd$_{23}$P$_{8}$]$^{2-}$ ($E_{1/2}$ = −0.83 V) and a reversible one-electron oxidation of Pd$_{23}$P$_{8}$/[Pd$_{23}$P$_{8}$]$^{+}$ ($E_{1/2}$ = 0.28 V). In light of the extremely facile conversion of Pd$_{23}$P$_{10}$ into Pd$_{23}$P$_{8}$, it is unclear whether its formation was induced electrochemically or by traces of air or other contaminations. The reduced [Pd$_{23}$P$_{10}$]$^{2-}$ form, [Pd$_{23}$(CO)$_{20}$(PEt$_3$)$_{10}$]$^{2-}$, has the same total number of valence electrons as that of the isolated Pd$_{23}$(CO)$_{21}$(PEt$_3$)$_{10}$ (with one additional CO ligand) and of the known isostructural heterometallic cluster, Au$_2$Pd$_{21}$(CO)$_{20}$(PEt$_3$)$_{10}$ (denoted as Au$_2$Pd$_{21}$), vide infra (Tran et al. 2004a). This latter Au$_2$Pd$_{21}$ cluster exhibits a CV consisting of two reversible one-electron reductions ($E_{1/2}$ = −1.19 and −1.42 V) and two reversible one-electron oxidations ($E_{1/2}$ = −0.05 and 0.28 V). Therefore, the total electron capacity of the isostructural 23-atom Pd$_{23}$ or Au$_2$Pd$_{21}$ clusters possessing a capped v$_2$-octahedral geometry changes over a range of six electrons from 288 for [Pd$_{23}$(CO)$_{20}$(PEt$_3$)$_{10}$]$^{2+}$ to 294 for [Au$_2$Pd$_{21}$(CO)$_{20}$(PEt$_3$)$_{10}$]$^{2-}$. Cyclic voltammograms of Pd$_{16}$(CO)$_{13}$(PMe$_3$)$_{9}$, Pd$_{35}$(CO)$_{23}$(PMe$_3$)$_{15}$ and Pd$_{39}$(CO)$_{23}$(PMe$_3$)$_{16}$ in THF showed no reductions out to −2.8 V and no oxidations out to +1.0 V (Tran et al. 2001).

5. Structural features and resulting implications

The observed structures of high-nuclearity transition metal carbonyl clusters ($n$ > 10) and, in particular, palladium CO/PR$_3$-ligated ones are the result of an energetic compromise between two trends: (i) maximization of M–M connectivities in a metal core (that per se leads to spheroidal-shaped geometries) and (ii) energy gain due to accommodation on the cluster surface of a certain number of ligands with certain steric requirements. Obviously, the concentrations of either the CO or PR$_3$ ligands play a critical role in cluster growth (vide supra). The steric/electronic properties of the PR$_3$ ligands per se are another factor that affects the metal-core shape and resulting metal nuclearity.

The PEt$_3$ ligand gives rise to the most diverse family of homopalladium Pd$_n$(CO)$_x$L$_y$ clusters, ranging in numbers of metal atoms per molecule from 4 to 145. Eleven distinctly different nanosized metal cores have been obtained; these include ones with face-centred cubic (FCC), commonly known as cubic close-packed (CCP) that are represented by Pd$_{23}$(CO)$_{20−22}$(PEt$_3$)$_{10}$ and
Pd_{30}(CO)_{26}(PEt_3)_{10}; mixed CCP/hexagonal close-packed (HCP) Pd_{52}(CO)_{36}(PEt_3)_{14}; Pd_{54}(CO)_{40}(PEt_3)_{14} and Pd_{66}(CO)_{45}(PEt_3)_{16}; highly deformed body-centred cubic (BCC) Pd_{23}(CO)_{20}(PEt_3)_{10}; single and interpenetrating icosahedral Pd_{16}(CO)_{13}(PEt_3)_{9} and Pd_{34}(CO)_{24}(PEt_3)_{12}, respectively; face-fused icosahedra Pd_{69}(CO)_{36}(PEt_3)_{18}; and the remarkable three-shell icosahedral structure of Pd_{145}(CO)_{x}(PEt_3)_{30}, x \sim 60. These structures are discussed below.

The Pd_{38}(CO)_{28}(PEt_3)_{12} cluster, which has a distorted interior Pd_4 tetrahedron, possesses a highly irregular core geometry and hence was not assigned to any of the above-mentioned structural types (Mednikov et al. 1987a).

6. Structures with cubic close and cubic close/hexagonal close packing

(a) General comments

The first example of a CCP Pd metal core was found in a monoclinic crystal form of Pd_{23}(CO)_{22}(PEt_3)_{10} (Mednikov et al. 1986). Its metal core and the disposition of the PEt_3 ligands are analogous to those in both the tetragonal and monoclinic crystal forms of Pd_{23}(CO)_{20}(PEt_3)_{10} (figure 2) and another monoclinic crystal form of Pd_{23}(CO)_{21}(PEt_3)_{10}. The metal core in each of these clusters is composed of a centred Pd_{19} ν_{2}-octahedron augmented by four wingtip Pd atoms. Phosphine ligand atoms are coordinated to all six vertices of the Pd_{19} octahedron and to the four wingtip Pd atoms. Accordingly, the Pd_{19} kernel may be envisioned as a centred hexa(square capped)-cuboctahedron with a(Pd_6) b(Pd_7) c(Pd_8) stacking layers. Note that n in the ν_{n}-designation denotes the number of M–M segments of neighbouring atoms along each edge.

(b) Variable CO ligations

The most remarkable feature of the CCP Pd_{19} kernel in these Pd_{23}(CO)_{x}(PEt_3)_{10} clusters is its ability to bind a variable different number of CO ligands: namely, x = 20, 21 and 22 (Mednikov et al. 2005a). The most stable compound, Pd_{23}(CO)_{20}(PEt_3)_{10}, possesses 20 CO’s (Wittayakun 2000) and is readily available through a number of different synthetic pathways. The x = 21 and 22 CO derivatives, Pd_{23}(CO)_{21}(PEt_3)_{10} and Pd_{23}(CO)_{22}(PEt_3)_{10}, are kinetically controlled products, and their isolation is challenging. The observed structures with variable CO coverage may be considered to represent X-ray snapshots of the dynamic behaviour of chemisorbed CO molecules on quasi-nanosized Pd{111} faces (figure 3).

(c) Structural changes in the Pd_{23} metal core chemically induced by variable PEt_3 ligations: reversible interconversion into highly different metal-core cubic close-packed/body-centred cubic geometries

Although varying degrees of CO coverage do not affect the Pd_{23} metal core of the Pd_{23}(CO)_{20}(PEt_3)_{10} cluster, the elimination of two PEt_3 ligands attached to its two Pd(apical) atoms (with retention of the 20 COs) results in dramatic geometrical changes, namely a transformation from a CCP (ν_{2}-octahedral Pd_{19} kernel) into the highly distorted body-centred structure of the Pd_{23}(CO)_{20}(PEt_3)_{8} cluster (figure 4) (Mednikov et al. 1987b). Nevertheless, the formation of the Pd_{23}P_{8} cluster can be rationalized if one takes into account the more spheroidal

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Review. Palladium CO/PR₃-ligated clusters

Figure 3. X-ray snapshots of CO ligation on two adjacent edge-fused ν₂ Pd₆ triangles in (a) Pd₂⁺(CO)₂₀(PEt₃)₁₀, (b) Pd₂⁺(CO)₂₁(PEt₃)₁₀ (front faces) and (c) Pd₂⁺(CO)₂₂(PEt₃)₁₀.

Figure 4. Comparative representation of two interconvertible highly dissimilar Pd₂³ clusters differed by two PEt₃ ligands (a) Pd₂⁺(CO)₂₀(PEt₃)₁₀ and (b) Pd₂⁺(CO)₂₀(PEt₃)₈. Two Pd atoms in apical positions in Pd₂³P₁₀ and their supposed positions in Pd₂³P₈ are shown in globe. CO ligands are in wire.

The shape of its metal core. Indeed, the accommodation of a smaller number of PEt₃ ligands about the metal framework with the same 23 Pd atoms requires the rearrangement of its shape in order to shrink the resulting surface for an effective protective-ligand coating. The two highly dissimilar Pd₂³ core geometries were shown conclusively from a ³¹P{¹H} NMR study to interconvert reversibly into each other (equation (6.1)) (Mednikov et al. 2003a)

\[
Pd_{23}(CO)_{20}(PEt_3)_{10} \overset{H^+ \text{ or } [O]}{\underset{2PEt_3}{\rightleftharpoons}} Pd_{23}(CO)_{20}(PEt_3)_{8}. \tag{6.1}
\]

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‘Twinned’ structures: cluster-growth patterns and yields

The geometry of Pd$_{30}$(CO)$_{26}$(PEt$_3$)$_{10}$ is closely related to that of Pd$_{23}$P$_{10}$ (Mednikov et al. 2003b). Its Pd$_{30}$ metal core of $C_{2h}$ symmetry with a maximum dimension of 1.1 nm is composed of two interpenetrating centred Pd$_{13}$ cuboctahedra, which form a ‘twinned’ Pd$_2$-centred Pd$_{20}$ bicuboctahedron with six common Pd atoms (figure 5). This Pd$_{20}$ bicuboctahedron is capped on six of eight square faces by six Pd atoms (four Pd(eq) and two Pd(ap)) and additionally edge-bridged by four (exopolyhedral) wingtip Pd atoms. These six additional Pd atoms give rise to a Pd$_{26}$ CCP fragment with an $a$(Pd$_6$) $b$(Pd$_7$) $c$(Pd$_7$) $a$(Pd$_6$) atom sequence. Ten PEt$_3$ ligands are distributed among six square-capped Pd atoms and four wingtip Pd atoms.

The Pd$_{54}$(CO)$_{40}$(PEt$_3$)$_{14}$ cluster of crystallographic $C_i$($ar{1}$) site symmetry was isolated together with Pd$_{30}$ (Mednikov et al. 2003b). Its metal-core architecture consists of a Pd$_{20}$ bicuboctahedron identical to that in Pd$_{30}$, thereby suggesting a similar aggregation pathway. However, further condensation of the next 20 Pd atoms gives rise to a Pd$_{40}$ fragment with mixed HCP/CCP stacking layers of $a$(Pd$_5$) $b$(Pd$_{10}$) $a$(Pd$_{10}$) $c$(Pd$_{10}$) $a$(Pd$_5$), resulting in encapsulation of six Pd atoms into a coplanar arrangement of four edge-fused equilateral triangles (figure 6a). The metal framework is completed by 14 additional face-capping Pd atoms, each having a PEt$_3$ ligand, to yield the final metal-core dimensions of $1.5 \times 1.2 \times 0.5$ nm (figure 6b). Its structure contains 32 doubly and 8 triply bridging carbonyl ligands.

The two structurally related mixed CCP/HCP metal cores of Pd$_{52}$(CO)$_{36}$(PEt$_3$)$_{14}$ (possessing maximum and minimum metal-core diameters of $1.6 \times 0.8$ nm) and Pd$_{66}$(CO)$_{45}$(PEt$_3$)$_{16}$ (possessing a maximum diameter of 1.1 nm) contain the same central vertex-truncated CCP Pd$_{38}$ kernel (figure 7b) as that of the unknown $v_3$ Pd$_{44}$ octahedron (figure 7a; Mednikov et al. 2005b). Although such Pd$_{38}$ and Pd$_{44}$ clusters are (as yet) unknown as distinct structural entities, analogous metal-core clusters of the congeneric Ni/Pt elements have been
Figure 6. (a) The HCP/CCP Pd_{40} metal core in the Pd_{54} cluster. Its Pd_{20} bicuboctahedron identical to that in Pd_{30} is shown in black. (b) The Pd_{54}P_{14} fragment of Pd_{54}(CO)_{40}(PEt_{3})_{14}.

preparing and structurally analysed; these include the vertex-truncated Pt_{38} core in [Pt_{38}(CO)_{44}]^{2-} (Chini 1980; Ceriotti et al. 1999), the v_{3}-octahedral Pt_{6}Ni_{38} core in [H_{6-n}Pt_{6}Ni_{38}(CO)_{18}]^{n-} (Ceriotti et al. 1985; de Biani et al. 1999; de Silva & Dahl 2006), the v_{3}-octahedral Pt_{9}Ni_{35} core in [Pt_{9}Ni_{35}(CO)_{48}]^{6-} (Femoni et al. 2004a) and the v_{3}-octahedral Pd_{8}Ni_{36} core in [Pd_{8}Ni_{36}(CO)_{48}]^{6-} (Femoni et al. 2004b). The common vertex-truncated Pd_{38} kernel of O_{h} symmetry in the Pd_{52} and Pd_{66} clusters encapsulates six octahedrally arranged Pd atoms and possesses six \{100\} square Pd_{4} faces and eight \{111\} centred hexagonal Pd_{7} faces (figure 7b). In both structures, condensation of the remaining Pd atoms occurs only on the \{111\} Pd_{7} faces via formal attachment of Pd-capped v_{2} Pd_{7} triangles. In the Pd_{66} cluster, four such fragments are condensed on four tetrahedrally oriented faces, whereas in the Pd_{52} cluster, condensation occurs on the two opposite faces. The decisive step is the sterically predetermined condensation of the second v_{2} Pd_{7} triangle that must occur only on the opposite face (as in the Pd_{52} cluster) or on any of the three symmetry equivalent tetrahedrally oriented faces of the Pd_{38} kernel (as in the Pd_{66} cluster). The probability of the condensation of this second Pd_{7} fragment on one of the latter sterically non-hindered faces of the Pd_{38} kernel is three times greater than on the opposite face, thus statistically favouring the formation of the Pd_{66} cluster over that of the Pd_{52} cluster (figures 8 and 9). This formal construction scheme is consistent with the observed good yield and reproducibility of the Pd_{66} cluster versus the low yield and problematic synthesis of the Pd_{52} cluster.

The total eight-layer metal-core stacking sequence of crystallographic \textit{C}_{3i} \text{(3)} symmetry in the Pd_{52} cluster is a(Pd) b(Pd_{6}) a(Pd_{7}) b(Pd_{12}) c(Pd_{12}) a(Pd_{7}) c(Pd_{6}) a(Pd) with eight interior Pd atoms arranged in a trans-bicapped
octahedron. In the $C_{3v}$ Pd$_{66}$ cluster, the metal-core stacking sequence, in which 10 Pd atoms of a tetrahedrally capped octahedron are encapsulated, depends on the (111) direction: along the proper $C_3$-axis it is $\text{abacba}$, while along the three other symmetry equivalent (111) directions, it is $\text{ababca}$.

Overall, the mean Pd–Pd connectivities in the Pd$_{30}$, Pd$_{52}$, Pd$_{54}$ and Pd$_{66}$ clusters composed of interpenetrating cuboctahedral building blocks are virtually identical at 2.81 Å. The Pd–Pd bonding connectivities in their encapsulated Pd$_m$ moieties are approximately 0.05 Å shorter, namely Pd$_{30}$ (Pd$_2$ dimer, 2.77 Å), Pd$_{52}$ (bicapped Pd$_8$ octahedron, 2.74 Å), Pd$_{54}$ (four coplanar edge-fused equilateral Pd$_6$ triangles, 2.76 Å) and Pd$_{66}$ (tetracapped Pd$_{10}$ octahedron, 2.75 Å); the mean for all four encapsulated moieties is 2.76 Å. Thus, the interior Pd atoms may be considered to have metallic character.

A salient structural feature of the neutral CCP Pd$_{23}$P$_{10}$, Pd$_{50}$ and mixed CCP/HCP Pd$_{52}$ and Pd$_{66}$ clusters is the augmentation of each {111} centred Pd$_7$ hexagon by a Pd-capped v$_2$ Pd$_7$P$_4$ triangle. Thus, the cluster growth is terminated along the (111) directions due to effective shielding by four phosphine ligands.

Figure 7. (a) Per se unknown v$_2$ Pd$_{44}$ octahedron. (b) Pd$_{38}$ kernel derived from vertex truncation of v$_2$ Pd$_{44}$ octahedron. Pd atoms to be truncated are shown in black.
Figure 8. (a) Condensation of the first two one-capped $v_2$ Pd$_7$ triangles on the two non-adjacent tetrahedrally oriented Pd-centred hexagons of Pd$_{38}$ kernel. Sterical availability of the two remaining non-adjacent centred hexagons gave rise to the Pd$_{66}$ cluster via addition of the next two Pd$_7$ fragments. (b) Pd$_{66}$P$_{16}$ fragment of Pd$_{66}$(CO)$_{45}$(PEt$_3$)$_{16}$. Pd atoms in Pd$_7$ fragments are in black.

Figure 9. (a) Condensation of the two Pd$_7$ fragments on the opposite Pd-centred hexagons of Pd$_{38}$ kernel with formation of Pd$_{52}$ cluster. Condensation of the next Pd$_7$ fragment is sterically forbidden. (b) Pd$_{52}$P$_{14}$ fragment of Pd$_{52}$(CO)$_{36}$(PEt$_3$)$_{14}$. Pd atoms in Pd$_7$ units are in black.
accompanied by doubly and triply bridging CO’s. In sharp contrast, in each of the heterometallic Pt−Ni and Pd−Ni carbonyl clusters possessing a vertex-truncated 38-atom $\nu_3$-octahedral $M_{38-x}M'_x$ kernel (vide supra), single-metal augmentation occurs on each $\{100\}$ square face. An exception is the $[\text{HPt}_{17}\text{Ni}_{24}(\text{CO})_{46}]^{5-}$ cluster (Femoni et al. 2004a), in which an Ni$_3$ triangle is attached to a Pt-centred Pt$_4$Ni$_3$ hexagon of the Pt$_{17}$Ni$_{21}$ kernel. In the Pt/Ni-disordered $[\text{Pt}_{24}\text{Ni}_{32}(\text{CO})_{56}]^{6-}$ cluster, all six $\{100\}$ square faces of the original Pt$_{38-x}$Ni$_x$ kernel are capped by Ni atoms; therefore, the observed further condensation of two Ni$_5$Pt $\nu_2$ triangles invariably occurs on open $\nu_3$-triangle faces, namely two opposite ones (Femoni et al. 2004a).

Concerning the coordination of bridging carbonyls, it should be noted that, in some structures, the borderline between $\mu_2$-CO and $\mu_3$-CO modes is blurred, thereby hampering a definitive assignment.

A rare case of a charged CO/PR$_3$-ligated nanosized homopalladium cluster is exemplified by the $[\text{Pd}_{29}(\text{CO})_{28}(\text{PPh}_3)_7]^{2-}$ dianion, in which the metal framework of pseudo-$C_{3v}$ symmetry encapsulates one interior atom in the third layer of a mixed HCP/CCP $\text{a}(\text{Pd}) \text{b}(\text{Pd}_3) \text{a}(\text{Pd}_{10}) \text{c}(\text{Pd}_{15})$ sequence (figure 10; Kawano et al. 2001).

(e) Heterometallic Au−Pd, Ni−Pd and Pt−Pd clusters

Two gold-containing analogues of Pd$_{23}$(CO)$_{20}$(PR$_3$)$_{10}$, namely, Au$_2$Pd$_{21}$(CO)$_{20}$(PR$_3$)$_{10}$ with R=Et, Me and the $[\text{AuPd}_{22}(\text{CO})_{20}(\text{PPh}_3)_4(\text{PMe}_3)_6]^{-}$ monoanion, were prepared under basic conditions from reactions of Au(PPh$_3$)$_2$Cl with either Pd(PR$_3$)$_2$Cl$_2$ or Pd$_{10}$(CO)$_{12}$(PEt$_3$)$_6$ (Tran et al. 2004a). The central interior position in both clusters is occupied by gold; in the Au$_2$Pd$_{21}$ cluster, the second gold atom is in an apical position in the centred Au$_2$Pd$_{17}$ $\nu_2$ octahedron.
The bimetallic Au−Pd cluster, \( \text{Au}_4\text{Pd}_{28}(\text{CO})_{22}(\text{PMe}_3)_{16} \), obtained from the reaction of \( \text{Pd}_{10}(\text{CO})_{12}(\text{PMe}_3)_{6} \) with \( \text{Au}(\text{PPh}_3)\text{Cl} \) or \( \text{Au}(\text{SMe}_2)\text{Cl} \), does not have a direct structural analogue with any CCP/HCP homopalladium cluster. Its \( \text{Au}_4\text{Pd}_{24} \) kernel with an encapsulated \( \text{Au}_4 \) tetrahedron is composed of four interpenetrating, highly distorted Au-centred cuboctahedra (figure 11; Mednikov et al. 2007a).

Two Ni−Pd anions, CCP \([\text{Pd}_{16}\text{Ni}_4(\text{CO})_{22}(\text{PPh}_3)_4]^2−\) and HCP \([\text{Pd}_{33}\text{Ni}_9(\text{CO})_{41}(\text{PPh}_3)_6]^4−\) (Kawano et al. 1996, 2001). The pseudo-\( \text{Td} \) \( \text{Pd}_{16}\text{Ni}_4 \) core is composed of a \( \nu_3 \) tetrahedron with Ni atoms at the four vertices (figure 12). The pseudo-\( \text{D}_{3h} \) \( \text{Pd}_{33}\text{Ni}_9 \) core can be envisioned as a five-layer structure of three alternating centred 10-atom \( \text{Pd}_7\text{Ni}_3 \) \( \nu_4 \) triangles (with Ni atoms at corner positions) and two six-atom \( \nu_2 \) \( \text{Pd}_6 \) triangles as follows: \( \text{a}(\text{Pd}_7\text{Ni}_3) \text{ b}(\text{Pd}_6) \text{ a}(\text{Pd}_7\text{Ni}_3) \text{ b}(\text{Pd}_6) \text{ a}(\text{Pd}_7\text{Ni}_3) \) (figure 13).

The structure of the hydrido Pt−Pd cluster, \( \text{H}_{12}\text{Pd}_{28}(\text{PtPMe}_3)(\text{PtPPh}_3)_{12}(\text{CO})_{27} \), contains a pseudo-\( \text{C}_3 \) \( \text{Pd}_{28}\text{Pt} \) kernel consisting of four HCP layers \( \text{a}(\text{Pd}_8) \text{ b}(\text{Pd}_7) \text{ a}(\text{Pd}_{12}) \text{ b}(\text{PtPd}_6) \) encapsulating \( \text{Pd}_4 \) tetrahedron (figure 14; Bemis & Dahl 1997). The 12 PPh$_3$-coordinated surface Pt atoms form PtPd$_5$ octahedra presumably occupied by H atoms.

7. Structures based on interpenetrating centred icosahedra

(a) General comments

Structures composed of centred interpenetrating icosahedra (II) have been observed in the \( \text{Pd}_n(\text{CO})_x(\text{PR}_3)_y \) family for \( n = 34, \text{R} = \text{Et}; \ n = 35, \text{R} = \text{Me}; \ n = 37, \text{R} = p\text{-Tolyl} \) and in heterometallic \( \text{PMe}_3 \)-ligated \( \text{Pd}_{29}\text{Ni}_3(\text{CO})_{22}(\text{PMe}_3)_{13} \)
Figure 12. Pd$_{16}$Ni$_4$P$_4$ fragment of [Pd$_{16}$Ni$_4$(CO)$_{22}$(PPh$_3$)$_4$]$^{2-}$ anion with $v_3$ tetrahedral metal core.

Figure 13. The Pd$_{33}$Ni$_9$P$_6$ fragment of [Pd$_{33}$Ni$_9$(CO)$_{41}$(PPh$_3$)$_6$]$^{4-}$ anion composed of four HCP layers a(Pd$_7$Ni$_3$) b(Pd$_6$) a(Pd$_7$Ni$_3$) b(Pd$_6$) a(Pd$_7$Ni$_3$).

(Tran et al. 2001) and Au$_2$Pd$_{41}$(CO)$_{27}$(PEt$_3$)$_{15}$ (Tran et al. 2004b). The possible aggregation sequence with experimentally observed metal kernels and corresponding conceptual scheme including up to five icosahedral units are shown in figures 15 and 16. The initial CO/PR$_3$-ligated single centred icosahedron was

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found in the $C_3$ symmetry cluster Pd$_{16}$(CO)$_{13}$(PR$_3$)$_9$ with R=Me (Tran et al. 2001), Et (Mednikov et al. 1991), both augmented with three wingtip Pd atoms (figure 17) and in the heterometallic [Au$_2$Pd$_{14}$(CO)$_9$(PMe$_3$)$_{11}$]$^{2+}$, containing a Pd-centred icosahedron, Au$_2$Pd$_{11}$, with an edge-condensed Pd$_5$ trigonal bipyramid (Copley et al. 1995). Although the Pd$_{19}$ double icosahedron (DI) per se is unknown, the pseudo-$C_{2v}$ Au$_5$Pd$_{45}$ core geometry of Au$_5$Pd$_{45}$(CO)$_{34}$(PEt$_3$)$_{14}$ (R. V. Nichiporuk, S. A. Ivanov & L. F. Dahl 2002, unpublished data) possesses a central 19-atom Au$_5$Pd$_{14}$ kernel consisting of two interpenetrating icosahedra (II) involving two centred Pd atoms, each coordinated to the central encapsulated Au$_5$-pentagon. DI skeletons, each composed of two twinned interpenetrating icosahedra (II) with seven common atoms, can be visualized in the Pd$_{23}$ kernel (with 3 DI) of Pd$_{37}$(CO)$_{28}$([p-Tolyl]$_3$)$_{12}$ (Mednikov & Dahl 2008), Pd$_{26}$ (with 6 DI) of Pd$_{29}$Ni$_3$(CO)$_{22}$(PMe$_3$)$_{13}$ and Pd$_{29}$ (with 9 DI) of Pd$_{35}$(CO)$_{23}$(PMe$_3$)$_{15}$ (Tran et al. 2001). In all three structures, a Pd–Pd bond between two interior atoms in each DI is also the edge of the encapsulated fragment that gives rise to a Pd$_3$ triangle in Pd$_{37}$, a Pd$_4$ tetrahedron in Pd$_{29}$Ni$_3$ and a Pd$_5$ trigonal bipyramid in Pd$_{35}$. The versatile PEt$_3$ ligand also stabilizes the interpenetrating icosahedra in Pd$_{34}$(CO)$_{24}$(PEt$_3$)$_{12}$ (Belyakova & Slovokhotov 2003); its Pd$_{26}$ kernel with an interior Pd$_4$ tetrahedron of four centred II that consist of six DIs is similar to that found in Pd$_{29}$Ni$_3$. Icosahedral building blocks in all of the aforementioned structures are distorted owing to large dispersions (approx. 0.3–0.9 Å) in tangential Pd$_{cage}$–Pd$_{cage}$ distances. Much less variations occur between radial Pd$_i$–Pd$_{cage}$ connectivitites that preserve the coordination number of 12 for each interstitial Pd$_i$ atom within its icosahedral environment.

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Figure 15. Proposed sequential growth pattern of interpenetrating icosahedra (II) consisting of interpenetrating double icosahedra (DI) includes metal kernels of (a) Pd₁₃ icosahedron as starting building block followed by (b) Pd₁₉, 1 DI; (c) Pd₂₃, 3 DI; (d) Pd₂₆, 6 DI; and (e) Pd₂₉, 9 DI. Atoms added in each separate step are shown in flat, encapsulated atoms in black. These distinctive metal kernels, except Pd₁₉, were found in Pd₁₆(CO)₁₃(PR₃)₉, R=Me, Et, one icosahedron; Pd₃₇(CO)₂₈{P(p-C₆H₄Me)₃}₁₂, 3 DI; Pd₂₉Ni₃(CO)₂₂(PMe₃)₁₃, 6 DI; Pd₃₄(CO)₂₄(PEt₃)₁₂, 6 DI; and Pd₃₅(CO)₂₃(PMe₃)₁₅, 9 DI.

The Au₂Pd₄₁(CO)₂₇(PEt₃)₁₅ cluster (obtained by thermolysis of Au₂Pd₂₁(CO)₂₀(PEt₃)₁₀ in THF) is related to Pd₃₅(CO)₂₃(PMe₃)₁₅ in that both have an interior five-atom trigonal bipyramidal geometry of Au₂Pd₃ and Pd₅, respectively (figure 18; Tran et al. 2004b). Furthermore, the three Pd₃ atoms of the Au₂Pd₃ trigonal bipyramid are equatorial and are the centres of the three II analogous to those in Pd₃₅. However, the coordination number of each of the two central gold atoms lying in apical positions is 13 instead of the classic 12. These two geometrically unprecedented 13-vertex Au-centred (μ₁₃-Au)Pd₁₃ polyhedra are face fused into the (μ₁₃-Au)₂Pd₂₃ fragment and related by a pseudo-σᵥ mirror plane passing through their common face of three equatorial Pd₃ atoms of the Au₂Pd₃ kernel. The entire Au₂Pd₄₁ framework includes this (μ₁₃-Au)₂Pd₂₃ fragment, which in turn is interpenetrated with three DI, Au₂Pd₂₁ (formed from three interpenetrating (μ₁₂-Pd)Au₂Pd₁₀ icosahedra) and completed with 12 capping Pd atoms.

(b) Cluster growth and analogy with double icosahedron models for charged Ar clusters

Of prime significance is that the number of atoms in the centred interpenetrating DI kernels of the Pd₃₇, Pd₂₉Ni₃ and Pd₃₅ clusters (vide supra) are exactly the same as those found (for that range) for dominant atom peaks
Figure 16. Conceptual view of the sequential growth process of interpenetrating icosahedra (II)/interpenetrating double icosahedra (DI) with formation of the 19-, 23-, 26-, and 29-atom members from a centred icosahedron (I) shown as a sphere.

Figure 17. Molecular structure of Pd$_{16}$(CO)$_{13}$(PR$_3$)$_9$, R=Me, Et, is the centred Pd$_{13}$ icosahedra with three wingtip Pd atoms, shown in black. CO ligands are in wire, R substituents omitted.

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of 23, 26 and 29 in the mass spectrum of charged argon clusters generated under low-temperature free-jet expansion (Harris et al. 1984). The growth pattern of interpenetrating DI, which gives rise to such numbers (depicted for Pd in figure 15), was proposed on the basis of maximization of connectivities between neighbouring atoms (Farges et al. 1985, 1988). The structural identity of experimentally observed interpenetrating Pd\textsubscript{23}, Pd\textsubscript{26} and Pd\textsubscript{29} DI with corresponding DI models for charged argon clusters provides compelling evidence for the distinctive role of *attractive dispersion interactions* in Pd\textsubscript{n} clusters with atoms in a closed-shell 5s\textsuperscript{0}4d\textsuperscript{10} configuration.
(c) Steric properties of ligands and metal-core shape

Several intriguing implications can be drawn from the comparative stereochemistry of the Pd\textsubscript{37}, Pd\textsubscript{29}Ni\textsubscript{3} and Pd\textsubscript{35} clusters. The experimentally documented normal packing mode for the larger encapsulated fragments requires a larger number of coating metal atoms. However, Pd\textsubscript{37}, in spite of having the largest total number of metal atoms [i.e. 37 relative to 32 in Pd\textsubscript{29}Ni\textsubscript{3} (interior Pd\textsubscript{4}) and 35 in Pd\textsubscript{35} (interior Pd\textsubscript{5})], encapsulates the smallest Pd\textsubscript{3} moiety. This anomalous trend results from the ligation by relatively bulky P(p-Tolyl)\textsubscript{3} ligands, which has a Tolman cone angle of 145° versus a much smaller cone angle of 118° for PMe\textsubscript{3} in the Pd\textsubscript{29}Ni\textsubscript{3} and Pd\textsubscript{35} clusters (Tolman 1977). Indeed, accommodation of 12 P(p-Tolyl)\textsubscript{3} ligands necessitates an extended surface, which is realized via the generation of a non-spheroidal Pd\textsubscript{37} metal core versus a spheroidal one of Pd\textsubscript{29}Ni\textsubscript{3} and a semi-spheroidal one of Pd\textsubscript{35}. An even more striking example is \([\text{Pd}\textsubscript{29}(\text{CO})\textsubscript{28}(\text{PPh}_{3})\textsubscript{7}]^{2-}\) (Kawano \textit{et al.} 2001) of mixed HCP/CCP packing (vide supra). This cluster with sterically the same phosphine ligand (i.e. the Tolman cone angles of 145° for PPh\textsubscript{3} and P(p-Tolyl)\textsubscript{3} are identical) encapsulates only one metal atom and therefore inevitably adopts an extended surface. The cluster is also CO enriched in order to protect the large metal-core surface, which has the relatively fewer number of PPh\textsubscript{3} ligands.

8. Structures with face-fused centred icosahedra

Two and three face-fused centred icosahedra of Pd\textsubscript{23} and Pd\textsubscript{33} were found in Pd\textsubscript{39}(CO)\textsubscript{23}(PMe\textsubscript{3})\textsubscript{16} (Tran \textit{et al.} 2001) and Pd\textsubscript{69}(CO)\textsubscript{36}(PEt\textsubscript{3})\textsubscript{18} (Tran & Dahl 2003), respectively. The former cluster, which is completed by condensation of 16 Pd atoms on its centred face-fused Pd\textsubscript{23} biicosahedron, possesses an encapsulated trigonal bipyramidal Pd\textsubscript{5} fragment, which is deformed from pseudo-$D_{3h}$ to a bent pseudo-$C_{2v}$ geometry (figure 19). In the Pd\textsubscript{69} metal core, three centred icosahedra are face-condensed via opposite faces. The middle icosahedron in the resulting linear Pd\textsubscript{33} tricosahedron is surrounded by a cyclic Pd\textsubscript{30} hexagonal tube composed of six Pd\textsubscript{7} centred hexagons each sharing their opposite edges. The remaining six Pd atoms cap six square faces between the Pd\textsubscript{33} tricosahedron and the hexagonal Pd\textsubscript{30} tube (figure 20). The interior fragment consists of 15 Pd atoms including the entire middle icosahedron and two centred Pd atoms from two neighbouring icosahedra. The maximal length/width dimensions of the Pd\textsubscript{69} nanosized metal core are $1.35 \times 0.92$ nm.

9. Other structural types involving centred icosahedral units or their fragments

In Pd\textsubscript{59}(CO)\textsubscript{32}(PMe\textsubscript{3})\textsubscript{21} of pseudo-$D_{3}$ symmetry (Tran \textit{et al.} 2001), two centred icosahedra ($\mu_{12}$-Pd)Pd\textsubscript{12} are separated by a Pd\textsubscript{3} triangle (figure 21). Due to the staggered orientation of the latter middle triangle, the resulting Pd\textsubscript{29} fragment can be viewed as a Pd\textsubscript{9} biocahedron face-fused along its threefold axis with two centred icosahedra. An additional 27 Pd atoms are attached to this Pd\textsubscript{29} fragment as face-fused octahedra and face-fused square pyramids. Each of the remaining three Pd atoms is connected to 10 Pd atoms and located on a twofold axis. The maximum linear size of the Pd\textsubscript{59} core along the principal threefold axis is approximately 1.3 nm.

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The icosahedral-based \( \text{Au}_4\text{Pd}_{32}(\text{CO})_{28}(\text{PMe}_3)_{14} \) was synthesized from the reaction of \( \text{Au}(\text{SMe}_2)\text{Cl} \) with \( \text{Pd}_{10}(\text{CO})_{12}(\text{PMe}_3)_6 \) (Mednikov & Dahl 2005). The \( \text{Au}_4 \) kernel in the \( \text{Au}_4\text{Pd}_{32} \) core may be considered as a highly distorted tetrahedron of pseudo-\( D_2 \) symmetry such that the three pairs of opposite equivalent edges are 2.64 Å (strongly bonding), 2.89 Å (secondary bonding) and 3.51 Å (non-bonding). Its geometry is predetermined by an icosahedral-based multi-twinned 36-atom metal framework of \( \text{Au}_4\text{Pd}_{32} \) (figure 22). The entire metal core may be viewed to arise from the specific interpenetration of two highly distorted double icosahedra each with one missing atom in its inner pentagon, i.e. \( \text{Au}_2\text{Pd}_{16} \), that is completed by four edge-bridged and two tetracapped Pd atoms.

A totally different polyicosahedral growth-sequence based on vertex-shared centred icosahedra, instead of interpenetrating or face-fused centred icosahedra in \( \text{Pd}_n(\text{CO})_x(\text{PR}_3)_y \) clusters (vide supra), was earlier established for
halide/phosphine-ligated Au−Ag and Au−Ag−M clusters (where M=Ni, Pd, Pt denote centred icosahedral M atoms; Teo & Zhang 1995). Nevertheless, the minimal (2 II, 1 DI) interpenetrating 19-atom unit is known for two nitrate/phosphine-ligated Au–Ag clusters, Au_{12}Ag_{7}(PMe_2Ph)_{10}(NO_3)_{9} and Au_{17}Ag_{2}(PMe_2Ph)_{10}(NO_3)_{9} (Nunokawa et al. 2005).

10. Multi-shell or ‘matryoshka’-like polyhedra of icosahedral symmetry

Two exceptional multi-shell clusters \( \text{Pd}_{145}(\text{CO})_x(\text{PEt}_3)_{30}, x \sim 60 \) (Tran et al. 2000b) and \((\mu_{12-\text{Pt}})\text{Pd}_{164-x}\text{Pt}_x(\text{CO})_{72}(\text{PPh}_3)_{20} (x \sim 7) \) (Mednikov et al. 2007b) were isolated and their icosahedral multi-shell polyhedra unambiguously established by X-ray crystallography. The \( \text{Pd}_{145} \) cluster was originally obtained from the reaction of \( \text{Pd}(\text{PEt}_3)_2\text{Cl}_2 \) with \( \text{Au}(\text{PPh}_3)\text{Cl} \) and later in higher yield.

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Figure 21. (a) A Pd$_{29}$ fragment of Pd$_9$ bioctahedron with its two opposite faces fused with two centred Pd$_{13}$ icosahedra. (b) Entire Pd$_{59}$P$_{21}$ fragment of Pd$_{59}$(CO)$_{32}$(PMe$_3$)$_{21}$. Pd atoms in Pd$_{29}$ fragment are in black, remaining ones in grey. CO and PMe$_3$ ligands are omitted.

Figure 22. (a) Au$_4$Pd$_{32}$(CO)$_{28}$L$_{14}$, L = PMe$_3$. (b) Its highly distorted tetrahedral Au$_4$ metal core with three pairs of opposite edges of $a = 2.64$ Å (average), $b = 2.89$ Å (average), and $c = 3.51$ Å (average). Pd atoms are in grey, Au spotted. CO ligands and Me substituents are omitted.
from Pd\textsubscript{10}(CO)\textsubscript{12}(PEt\textsubscript{3})\textsubscript{6} (N. T. Tran & L. F. Dahl 2003, unpublished data). The second 165-atom Pd–Pt cluster was isolated from the short-time thermolysis of Pd\textsubscript{10}(CO)\textsubscript{12}(PPh\textsubscript{3})\textsubscript{6} in the presence of Pt(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} in THF, 30 min at 65°C.

The similar geometries of the first three shells in these M\textsubscript{145} and M\textsubscript{165} clusters are composed of a centred icosahedron (\(\mu\textsubscript{12-M}\)M\textsubscript{12}) that is encapsulated by a 42-atom \(\nu\textsubscript{2}\) icosahedron, which in turn is surrounded by a 60-atom rhombicosidodecahedral cage (vide infra). This latter semi-regular polyhedron (i.e. more than one type of polygon) consists of 12 pentagonal, 20 triangular and 30 square faces. Its square faces in the Pd\textsubscript{145} cluster are capped with 30 Pd atoms, whereas in the M\textsubscript{165} cluster, both the square and triangular faces are occupied by capping atoms to form the fourth shell, namely, a 50-atom \(\nu\textsubscript{2}\) pentagonal dodecahedron (figure 23).

The total number of approximately eight Pt atoms in the M\textsubscript{165} crystals was obtained from an X-ray Pt/Pd microanalysis and is in accordance with the crystallographic data that revealed the central atom to be pure Pt, with the others distributed among the first three shells as follows: first shell with Pt\textsubscript{x}Pd\textsubscript{12-x} cage, \(x \sim 1.2\); second shell with Pt\textsubscript{x}Pd\textsubscript{42-x} cage, \(x \sim 3.5\); and third shell with Pt\textsubscript{x}Pd\textsubscript{60-x} cage, \(x \sim 2.2\).

There are several important stereochemical features that should be emphasized. The shells above the 55-atom two-shell icosahedron in both clusters are atom-deficient. In fact, the third shell, if it were in accordance with the proposed normal icosahedral growth (Mackay 1962), should be a 92-atom \(\nu\textsubscript{3}\) icosahedron arising from an edge-capping/vertex arrangement (upon all \(\nu\textsubscript{2}\) triangles of the second shell) with an abca CCP sequence along threefold axes. Instead, the third...
shell in the Pd$_{145}$ and M$_{165}$ clusters is formed by face-capping of three threefold related triangles in each of the 20 icosahedral M$_6$ faces of the second shell (abcb (CCP–HCP)-sequence) that gives rise to a 60-atom polyhedron of the so-called twinned or anti-Mackay arrangement (Farges et al. 1986, 1988; Northby 1987; Doye & Wales 1997).

Geometrically, encapsulation of the second 42-atom shell by an atom-deficient 60-atom shell inevitably requires elongation of at least one-half of its M–M connectivities. Indeed, in the M$_{165}$ cluster, all 120 M–M edge connectivities of its M$_{60}$ Archimedean polyhedron are 3.0 Å, which noticeably exceeds the normal Pd–Pd bond length of 2.7–2.8 Å. On the other hand, in the Pd$_{60}$ polyhedron of the third shell of the Pd$_{145}$ cluster, only 60 pentagon/square edges are elongated up to 3.1 Å, whereas the other 60 triangle/square edges are 2.8 Å. The observed rectangular geometry of all 30 tetragons makes the Pd$_{60}$ polyhedron non-Archimedean (by definition) but yet with retention of pseudo-I$_h$ symmetry.

Formation and stabilization of the 50-atom $n_2$ pentagonal dodecahedral fourth shell in M$_{165}$ is induced by relatively bulky PPh$_3$ ligands (versus smaller PEt$_3$ ligands in Pd$_{145}$) providing an effective protection. This shell, in turn, creates an equalizing effect on tangential connectivities in the previous M$_{60}$ shell. Its 20 vertex Pd atoms with attached PPh$_3$ ligands cap triangular faces of the Archimedean M$_{60}$ cage, whereas the remaining middle-edge atoms cap 30 square faces. This 50-atom pentagonal dodecahedral shell is even more atom-deficient, but amazingly regular with the narrow range of Pd–Pd distances, i.e. 3.07–3.11 Å; average, 3.10 Å. Its large open pentagons with the edge length of 6.2 Å give rise to the overall dimple-ball shape of the M$_{165}$ metal core and greatly facilitate the intershell CO-bridged coordination.

The pseudo-I$_h$ symmetry of the Pd$_{145}$ and M$_{165}$ clusters may also be viewed as five-shell and six-shell $n_1$ polyhedra, in which all atoms in each shell occupy equivalent vertex positions and therefore are equally distanced from the central atom (Alvarez 2005). In this way, the M$_{165}$ cluster may be alternatively designated as Pt@M$_{12}$(icosahedron)@M$_{30}$(icosidodecahedron)@M$_{12}$(icosahedron)@M$_{60}$(rhomboicosidodecahedron)@M$_{30}$(icosidodecahedron)@M$_{20}$(pentagonal dodecahedron). The maximum diameters of the Pd$_{145}$ and M$_{165}$ metal cores are 1.65 and 1.73 Å, respectively.

11. Conclusions

The astonishing diversity of structural types and distinguished reactivities of large palladium carbonyl clusters stabilized by PR$_3$ ligands are proposed to be a consequence of the relatively weak Pd–L and zerovalent Pd–Pd bonds. In fact, because of the 5s$^0$4d$^{10}$ closed-shell ground-state configuration of atomic palladium, the Pd(0)–Pd(0) interactions are the weakest among the zerovalent metals of the Ni triad coupled with normally weak Pd(0)–CO bonding (Mednikov & Dahl 2009). In sharp contrast to normally strong Ni–CO and Pt–CO bonding, the relatively weak Pd–CO bonding may be readily ascribed to small metal-to-ligand electron transfer involving greatly reduced CO back bonding. Yet, the controlled growth of many of these clusters is realized via the appropriate choice of deligation reagents, as well as thoroughly adjusted reaction
conditions. Complementary synthetic pathways include fragmentation and comproportionation reactions, and spontaneous growth via disproportionation reactions. Regardless of the synthetic methods employed, the nuclearity and shape of the products are dictated by both kinetic conditions and steric/electronic properties of PR₃ ligands. For many of these clusters, reasonably good yields were ultimately achieved by optimization of the reaction conditions and, in some cases, by the structure-to-synthesis approach involving the designed use of different structurally suggested synthetic pathways.

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