

# Synthesis of large palladium clusters. The preparation of $\text{Pd}_{38}(\text{CO})_{28}(\text{PR}_3)_{12}$ ( $\text{R} = \text{Et}, \text{Bu}^n$ ) and $\text{Pd}_{34}(\text{CO})_{24}(\text{PEt}_3)_{12}$

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Several methods for the synthesis of the  $\text{Pd}_{38}(\text{CO})_{28}\text{L}_{12}$  cluster ( $\text{L} = \text{PEt}_3$ ) by treatment of  $\text{Pd}_{10}(\text{CO})_{12}\text{L}_6$  with  $\text{CF}_3\text{COOH}-\text{Me}_3\text{NO}$ ,  $\text{CF}_3\text{COOH}-\text{H}_2\text{O}_2$ ,  $\text{Pd}(\text{OAc})_2-\text{Me}_3\text{NO}$ , and  $\text{Pd}_2(\text{dba})_3$  mixtures (dba is dibenzylideneacetone) were proposed. The tri-*n*-butylphosphine analog,  $\text{Pd}_{38}(\text{CO})_{28}(\text{PBu}_3)_{12}$ , was synthesized by the reaction of  $\text{Pd}_{10}(\text{CO})_{14}(\text{PBu}_3)_4$  with  $\text{Me}_3\text{NO}$ . The reaction of  $\text{Pd}_4(\text{CO})_5\text{L}_4$  with  $\text{Pd}_2(\text{dba})_3$  yields clusters with an icosahedral packing of the metal atoms,  $\text{Pd}_{34}(\text{CO})_{24}\text{L}_{12}$  and  $\text{Pd}_{16}(\text{CO})_{13}\text{L}_9$ .

**Key words:** palladium, carbonylphosphine clusters, synthesis.

The methods for the synthesis of a series of individual palladium clusters containing an intrapolyhedral metal atom, viz.,  $\text{Pd}_{16}(\text{CO})_{13}\text{L}_9$  (**1**),  $\text{Pd}_{23}(\text{CO})_{22}(\text{PR}_3)_{10}$  (where  $\text{R} = \text{Et}$  and  $\text{Bu}$ ), and  $\text{Pd}_{23}(\text{CO})_{20}\text{L}_8$  (**3**), have been described earlier.<sup>1</sup>

The purpose of the present work is to develop procedures for the synthesis of two other large clusters,  $\text{Pd}_{38}(\text{CO})_{28}\text{L}_{12}$  (**4**) and  $\text{Pd}_{34}(\text{CO})_{24}\text{L}_{12}$  (**5**), which contain several intrapolyhedral atoms. Earlier, complex **4** was obtained in a low yield<sup>2</sup> by the reaction of  $\text{Pd}_{10}(\text{CO})_{12}\text{L}_6$  (**6**) with  $\text{Pd}(\text{OAc})_2$ . This reaction usually yields a mixture of two, three, or four clusters, sometimes containing **5**. The structures of complexes **4** and **5** were established by X-ray analysis\* (the structure of **4** is described in Ref. 2).

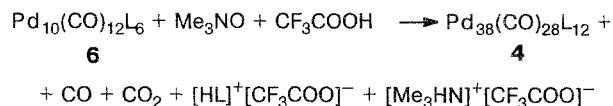
We have investigated the reactions of the clusters **6**,  $\text{Pd}_4(\text{CO})_5\text{L}_4$  (**7**), and  $\text{Pd}_{10}(\text{CO})_{12}\text{L}'_6$  ( $\text{L}' = \text{PBu}_3$ ) (**8**) with  $\text{CF}_3\text{COOH}$ ,  $\text{H}_2\text{O}_2$ , air,  $\text{Pd}_2(\text{dba})_3$ , and  $\text{CF}_3\text{COOH}-\text{Me}_3\text{NO}$ ,  $\text{CF}_3\text{COOH}-\text{H}_2\text{O}_2$ , and  $\text{Pd}(\text{OAc})_2-\text{Me}_3\text{NO}$  mixtures in an inert atmosphere.

The above-mentioned reagents are capable of binding ligands through oxidation ( $\text{Me}_3\text{NO}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$ ), protonation ( $\text{CF}_3\text{COOH}$ ), or complexation ( $\text{Pd}(\text{OAc})_2$  and  $\text{Pd}_2(\text{dba})_3$ ). Since the elimination of even one molecule from the ligand environment of a cluster results in enlargement of this cluster, all of these ways are effective. The main difficulty is finding the conditions, which cannot be predicted, for obtaining the individual compounds. This problem is complicated by the formation

of a rather great number of reaction products that have ligand environments of the same type, although their metal polyhedra have different structures. Up to now, six such "islands of stability" with nuclearity  $n > 10$  have been found only by X-ray analysis.

These reactions show a clear dependence on kinetic factors. This fact made it possible to find the conditions for obtaining compounds in the individual state using a significant number of deliganding agents.

The results of deliganding *via* treatment with  $\text{CF}_3\text{COOH}$  and a  $\text{CF}_3\text{COOH}-\text{Me}_3\text{NO}$  mixture are given in Table 1. The reaction with  $\text{CF}_3\text{COOH}$  usually yields no solid crystalline products, and the addition of  $\text{Me}_3\text{NO}$  is necessary to form crystals of the carbonylphosphine clusters.



To obtain cluster **4** in the individual state, the following conditions must be fulfilled: the ratio **6** :  $\text{Me}_3\text{NO}$  must be (1 : 4)–(1 : 16) and  $\text{Me}_3\text{NO}$  :  $\text{CF}_3\text{COOH}$  must be (1 : 2)–(1 : 4). Low (see Table 1, entry 4) and high concentrations of  $\text{Me}_3\text{NO}$  and  $\text{CF}_3\text{COOH}$  (entries 17, 20–23), as well as concentrations of  $\text{Me}_3\text{NO}$  higher than those of  $\text{CF}_3\text{COOH}$  (entries 18 and 19) are unsuitable. In addition, the reaction is sensitive to the actual concentration of CO. Thus, even a single elimination of the CO generated results in a mixture of clusters (see Table 1, entries 5–7, 9, 12, 13).

Tetramer **7** may also be used as a starting compound for synthesizing cluster **4** (entry 25).

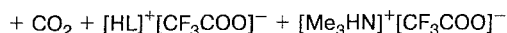
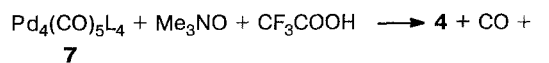
\* X-ray structure analysis was performed by Yu. L. Slovokhotov and Yu. T. Struchkov (A. N. Nesmeyanov Institute of Organoelement Compounds of the RAS).

**Table 1.** Synthesis conditions, yields and compositions of the products of the reaction of cluster **6** with CF<sub>3</sub>COOH and Me<sub>3</sub>NO

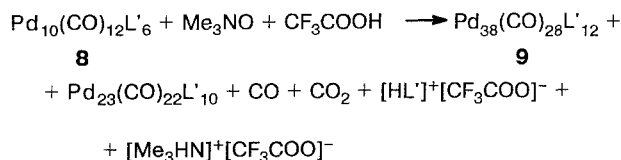
Entry	<b>6</b> : CF <sub>3</sub> COOH	<b>6</b> : Me <sub>3</sub> NO	$\tau_r$ /day	Composition of the crystalline products (%) [yield (%)]					Unidentified compounds
				1	2	3	4	5	
1	1 : 5	—	—	—	—	—	—	—	—
2	1 : 30	—	—	—	—	—	100 [58]	—	—
3	1 : 40	—	1	—	—	—	—	—	—
4	1 : 5	1 : 0.5	—	—	—	—	—	—	—
5	1 : 5	1 : 0.5	7	—	23 [15]	—	70 [51]	7 [5]	—
6	1 : 40	1 : 3	0.2**	—	—	30 [18]	10 [6]	—	60 [37]
7	1 : 5	1 : 4	5	—	—	—	79 [49]	—	21 [16]***
8	1 : 10	1 : 4	—	—	—	—	100 [45]	—	—
9	1 : 10	1 : 4	0.04	—	24 [10]	—	76 [35]	—	—
10	1 : 30	1 : 4	—	—	—	—	100 [61]	—	—
11	1 : 10	1 : 8	—	—	—	—	100 [38]	—	—
12	1 : 10	1 : 8	0.04	20 [14]	71 [54]	—	6 [5]	3 [2.5]	—
13	1 : 10	1 : 8	1	—	—	—	25 [7]	25 [7]	50***
14	1 : 30	1 : 8	—	—	—	—	100 [50]	—	—
15	1 : 70	1 : 8	—	—	—	—	100 [34]	—	—
16	1 : 30	1 : 16	—	—	—	—	100 [50]	—	—
17	1 : 120	1 : 16	—	—	—	—	—	—	100 [42]
18	1 : 10	1 : 20	—	—	—	—	—	—	100[88]***
19	1 : 10	1 : 20	—	27 [9]	—	—	—	—	73***
20	1 : 60	1 : 30	—	—	—	—	81 [46]	—	19
21	1 : 120	1 : 30	—	—	—	—	—	—	100 [32]
22	1 : 120	1 : 60	—	—	—	—	15 [6]	—	85
23	1 : 240	1 : 60	—	—	—	—	—	—	100 [44]
24*	1 : 12	—	—	—	—	—	—	—	—
25*	1 : 40	1 : 10	—	—	—	—	100 [22]	—	—

Note. For 0.095 mmol of **6**; Me<sub>2</sub>CO (7 mL) + Et<sub>2</sub>O (2 mL) as the solvent;  $\tau_r$  is time from the beginning of the reaction to the renewal of the atmosphere; volume of the gas phase was 120 mL; duration of the experiments was 7–17 days. Compounds were isolated as crystals, separated mechanically and identified by the IR spectra.

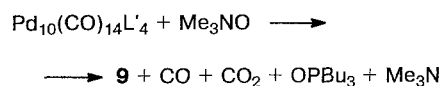
\* Starting cluster **7** (0.2 mmol). \*\* With subsequent crystallization in the presence of water vapor. \*\*\* Amorphous.



However, the replacement of PEt<sub>3</sub> with PBu<sub>3</sub> does not yield Pd<sub>38</sub>(CO)<sub>28</sub>L'<sub>12</sub> (**9**) as a separate compound even under the conditions that were found to be optimal. In the case of the ratio **8** : Me<sub>3</sub>NO : CF<sub>3</sub>COOH = 1 : 8 : 30, a mixture of clusters **9** and Pd<sub>23</sub>(CO)<sub>22</sub>L'<sub>10</sub> containing starting **8** formed. The ratio between the components of the mixture depends on many factors and is not easily controlled.

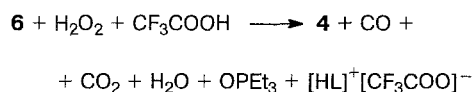


It was possible to obtain cluster **9** from another decanuclear isomer, Pd<sub>10</sub>(CO)<sub>14</sub>L'<sub>4</sub>, by the treatment with 2 equiv. of Me<sub>3</sub>NO in the absence of CF<sub>3</sub>COOH.

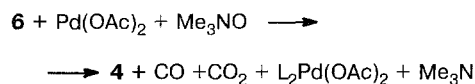


The IR spectrum of cluster **9** exhibits the same set of absorption bands as the spectrum of **4**.

The salient feature of the synthesis of cluster **4** by the oxidation of complex **6** with hydrogen peroxide and a CF<sub>3</sub>COOH–H<sub>2</sub>O<sub>2</sub> mixture is the narrower range of suitable concentrations, *i.e.*, the ratio **6** : H<sub>2</sub>O<sub>2</sub> : CF<sub>3</sub>COOH = 1 : 1 : (5–10) (Table 2). The oxidation of cluster **6** by air results in a similar set of products.



Still more stringent requirements for the ratio of the reagent concentrations are necessary for the synthesis of cluster **4** by treatment with Pd(OAc)<sub>2</sub> and Me<sub>3</sub>NO, *viz.*, **6** : Pd(OAc)<sub>2</sub> : Me<sub>3</sub>NO = 1 : 3 : 1.



The most convenient procedure for the synthesis of cluster **4** is the reaction of **6** with a CF<sub>3</sub>COOH–Me<sub>3</sub>NO mixture.

An investigation of the products of the reaction of complex **6** with Pd<sub>2</sub>(dba)<sub>3</sub> revealed the preferential for-

**Table 2.** Synthesis conditions, yields and compositions of the products of the reaction of cluster **6** with H<sub>2</sub>O<sub>2</sub>, CF<sub>3</sub>COOH, and air

Entry	<b>6</b> : H <sub>2</sub> O <sub>2</sub>	<b>6</b> : CF <sub>3</sub> COOH	Composition of the crystalline products (%) [yield (%)]		
			<b>2</b>	<b>4</b>	Unidentified compounds
1	1 : 0.1	—	100 [13]	—	—
2	1 : 0.3	—	100 [15]	—	—
3	1 : 2.5	—	11 [4]	89 [36]	—
4	1 : 6.0	—	—	93 [43]	7**
5	1 : 0.5	1 : 5	34 [14]	53 [26]	13
6	1 : 1	1 : 2.5	35 [17]	65 [35]	—
7	1 : 1	1 : 5	—	100 [49]	—
8	1 : 1	1 : 10	—	100 [49]	—
9	1 : 2	1 : 20	—	30 [16]	70**
10*	—	—	—	95 [42]	5**

Note. Duration of the reactions was 5–10 days, volume of the gas phase was 40–100 mL. For the other conditions, see the note in Table 1.

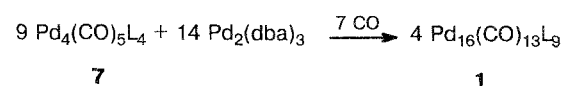
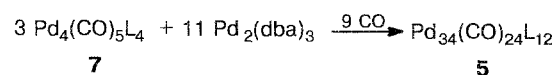
\* Oxidizing agent is air. \*\* Amorphous.

mation of cluster **5** when the **6** : Pd<sub>2</sub>(dba)<sub>3</sub> ratio was (1 : 2.5)–(1 : 3) (Table 3, entries 4–7). The polyhedron of this compound consists of reciprocally penetrating icosahedra. Additions of Me<sub>3</sub>NO and HOAc or the removal of CO decrease the selectivity of the reaction. If the reaction is carried out in the absence of Et<sub>2</sub>O, a single product, **4**, is formed (see Table 3, entries 9–13). The yields obtained indicate that Pd<sub>2</sub>(dba)<sub>3</sub> not only acts as a ligand acceptor, but to a lesser degree in a series of cases the metal atoms of the dibenzylidene complex are included in the formed compounds.

Cluster **5** was synthesized by the reaction of complex **7** with 3 equiv. of Pd<sub>2</sub>(dba)<sub>3</sub>. Using half this amount of

Pd<sub>2</sub>(dba)<sub>3</sub> gives Pd<sub>16</sub>(CO)<sub>13</sub>L<sub>9</sub>. It is of interest to note that in both cases compounds with icosahedral packing are obtained.

The reasons for the formation of clusters **5** and **1** are partially associated with the stoichiometry of the reactions under conditions of a deficiency of CO.

**Table 3.** Synthesis conditions and compositions of the products of the reactions of clusters **6** and **7** with Pd<sub>2</sub>(dba)<sub>3</sub>

Entry	<b>6</b> : Pd <sub>2</sub> (dba) <sub>3</sub>	<b>7</b> : Pd <sub>2</sub> (dba) <sub>3</sub>	<b>6</b> : Me <sub>3</sub> NO	HOAc /mL	τ <sub>r</sub> /h	Composition of the crystalline products (%)				Total yield (%)
						<b>1</b>	<b>2</b>	<b>4</b>	<b>5</b>	
1	1 : 1	—	—	—	—	—	44	35	21	70
2	1 : 1.3	—	—	—	—	—	46	50	4	77
3	1 : 2	—	—	—	—	—	44	44	12	98
4	1 : 2.5	—	—	—	—	—	—	—	100	119
5	1 : 2.5	—	—	—	—	—	11	—	89	125
6	1 : 3	—	—	—	—	—	—	9	91	132
7	1 : 3	—	—	—	—	—	12	12	76	147
8*	1 : 5	—	—	—	—	—	—	7***	—	59
9	1 : 2.5	—	—	—	1; 5	—	33	5	62	132
10	1 : 2.5	—	1 : 3	—	—	—	4	60	36	81
11	1 : 2.5	—	1 : 1.5	0.05	—	—	4	37	59	99
12	1 : 2.5	—	1 : 1.5	0.3	5	—	11	26	63	133
13**	1 : 2.5	—	—	—	—	—	—	100	—	94
14	—	1 : 1.5	—	—	—	100	—	—	—	102
15	—	1 : 3	—	—	—	—	—	—	100	58

Note. For 0.062 mmol of **6** and 0.08 mmol of **7**; volume of the gas phase was 40–60 mL; duration of the experiments was 4–14 days. For the total yields are given relative to **6** or **7**, respectively. For the other conditions, see the note in Table 1.

\* Dissolved with heating at 40 °C. \*\* In the absence of Et<sub>2</sub>O. \*\*\* In addition to complex **4**, 50 mg (55 %) of a black amorphous precipitate was isolated. For this compound, found (%): Pd, 72.0; P, 3.0.

Of the Pd carbonylphosphine clusters containing in-trapolyhedral metal atoms, clusters **5** and **1** have ligand spheres with the lowest number of CO groups.

We know only one example of the use of Pd di-benzylidene complexes for the synthesis of carbonylphosphine compounds, viz., the synthesis of  $\text{Pd}_8(\text{CO})_8(\text{PMe}_3)_7$  by the reaction of  $\text{Pd}(\text{dba})_2$  with  $\text{PMe}_3$  and CO.<sup>3</sup>

### Experimental

The grades of the reagents and the methods for the synthesis and analysis of the compounds are described in our previous work<sup>1</sup> (see also references herein). The  $\text{Pd}_2(\text{dba})_3$  complex (see Ref. 4) was recrystallized from a  $\text{CHCl}_3$ –heptane mixture. The concentration of  $\text{H}_2\text{O}_2$  ("pure for analysis" grade) was monitored by permanganometry. All of the reactions were performed in an argon atmosphere. IR spectra were recorded on a Specord M80 spectrophotometer using samples suspended in vaseline oil in an argon atmosphere.

**Synthesis of cluster 4. A. The reaction of complex 6 with  $\text{CF}_3\text{COOH}$  and  $\text{Me}_3\text{NO}$ .** A mixture of **6** (0.200 g, 0.095 mmol) and  $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$  (0.042 g, 0.378 mmol) was dissolved in a mixture of  $\text{Me}_2\text{CO}$  (7.5 mL),  $\text{Et}_2\text{O}$  (1.5 mL), and  $\text{CF}_3\text{COOH}$  (0.20 mL, 2.70 mmol) at 30 °C and stored for 17 days at room temperature. The precipitate of black crystals was washed with  $\text{Me}_2\text{CO}$  and  $\text{Et}_2\text{O}$  and dried *in vacuo*. Cluster **4** was obtained in 0.096 g (61 %) yield. Found (%): Pd, 64.37; P, 5.82.  $\text{C}_{100}\text{H}_{180}\text{O}_{28}\text{P}_{12}\text{Pd}_{38}$ . Calculated, (%): Pd, 64.74; P, 5.95. IR,  $\nu(\text{CO})/\text{cm}^{-1}$ : 1899 s, 1885 s–m, 1849 s, 1842 s–m, 1817 m sh, 1778 w.

**B. The reaction of complex 7 with  $\text{CF}_3\text{COOH}$  and  $\text{Me}_3\text{NO}$ .** Compound **7** (0.217 g, 0.209 mmol) and  $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$  (0.232 g, 2.087 mmol) were stirred in a mixture of  $\text{Me}_2\text{CO}$  (7 mL),  $\text{Et}_2\text{O}$  (2 mL), and  $\text{CF}_3\text{COOH}$  (0.62 mL, 8.37 mmol) for 10 min at 30 °C and stored for 8 days at room temperature. The precipitate of black crystals was washed with  $\text{Me}_2\text{CO}$  and dried in a flow of Ar. The yield of cluster **4** was 0.031 g (22 %). IR,  $\nu(\text{CO})/\text{cm}^{-1}$ : 1899 s, 1885 m, 1850 s, 1840 m, 1817 w.

**C. The reaction of complex 6 with  $\text{CF}_3\text{COOH}$  and  $\text{H}_2\text{O}_2$ .** A mixture of  $\text{Me}_2\text{CO}$  (7 mL),  $\text{Et}_2\text{O}$  (2 mL),  $\text{CF}_3\text{COOH}$  (0.07 mL, 0.945 mmol), and a 2.15 % solution of  $\text{H}_2\text{O}_2$  (0.15 mL, 0.095 mmol) was added to compound **6** (0.200 g, 0.095 mmol). The reaction mixture was stirred until dissolution and stored for 7 days at room temperature. Cluster **4** was obtained in 0.076 g yield as black crystals. The IR spectrum was identical to that of cluster **4** prepared by procedures **A** and **B**.

**D. The reaction of complex 6 with  $\text{Pd}(\text{OAc})_2$ .** A mixture of **6** (0.200 g, 0.095 mmol),  $\text{Pd}(\text{OAc})_2$  (0.064 g, 0.285 mmol), and  $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$  (0.011 g, 0.099 mmol) was dissolved in a

mixture of  $\text{Me}_2\text{CO}$  (7.4 mL),  $\text{Et}_2\text{O}$  (1.6 mL), and  $\text{EtOH}$  (0.3 mL) and stored for 8 days at room temperature. Cluster **4** (0.085 g) was obtained as black crystals in 54 % yield. The IR spectrum was identical to that of cluster **4** prepared by the above described procedures.

**Synthesis of cluster 5. A. Reaction of 6 with  $\text{Pd}_2(\text{dba})_3$ .** A mixture of **6** (0.130 g, 0.062 mmol) and  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (0.160 g, 0.155 mmol) was dissolved in a mixture of  $\text{Me}_2\text{CO}$  (7 mL) and  $\text{Et}_2\text{O}$  (2 mL) and stored for 4 days at room temperature. The precipitate of black flakes was washed with  $\text{Me}_2\text{CO}$  and dried in a flow of Ar. The yield of cluster **5** was 0.123 g (119 %). Found (%): Pd, 62.93; P, 6.40.  $\text{C}_{96}\text{H}_{180}\text{O}_{24}\text{P}_{12}\text{Pd}_{34}$ . Calculated (%): Pd, 63.38; P, 6.51. IR,  $\nu(\text{CO})/\text{cm}^{-1}$ : 1892 s, 1865 s, 1837 s, 1809 s–m.

Analogously, but in the absence of  $\text{Et}_2\text{O}$ , cluster **4** (0.095 g) was obtained in 94 % yield as black crystals identified by its IR spectrum.

**B. Reaction of 7 with  $\text{Pd}_2(\text{dba})_3$ .** Cluster **7** (0.082 g, 0.079 mmol) and  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (0.245 g, 0.237 mmol) were stirred in a mixture of  $\text{Me}_2\text{CO}$  (7 mL) and  $\text{Et}_2\text{O}$  (2 mL) at 30 °C until most of the solids were dissolved. The reaction mixture was stored for 5 days at room temperature. The precipitate of black flakes and finely divided crystals was washed with  $\text{Me}_2\text{CO}$  and dried in a flow of Ar. The yield of cluster **5** was 0.031 g (58 %) and the yield of  $\text{Pd}(\text{dba})_2$  was 0.041 g. The IR spectrum of **5**,  $\nu(\text{CO})/\text{cm}^{-1}$ : 1893 s, 1865 s, 1836 s, 1809 s, 1756 w. The IR spectrum of  $\text{Pd}(\text{dba})_2$  (tablets with KBr),  $\nu/\text{cm}^{-1}$ : 1645 (C=O); 1617 (C=C<sub>aliph</sub>); 1578 (C=C<sub>arom</sub>); 1545 (C=C<sub>arom</sub>).

**Synthesis of cluster 9.** A mixture of  $\text{Pd}_{10}(\text{CO})_{14}\text{L}_4$  (0.200 g, 0.088 mmol) and  $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$  (0.020 g, 0.180 mmol) was dissolved in a mixture of  $\text{Me}_2\text{CO}$  (6 mL) and  $\text{EtOH}$  (1 mL). After 3 h, the atmosphere was renewed by introducing another portion of Ar. After an additional 24 h, the atmosphere was repeatedly renewed, and the solution was stored under the  $\text{EtOH}$ – $\text{H}_2\text{O}$  vapor liberated by a 1 : 6  $\text{H}_2\text{O}$ – $\text{EtOH}$  mixture. After an additional 3 days, the black crystals that formed were washed with  $\text{EtOH}$  and dried *in vacuo*. The yield of cluster **9** was 0.046 g (27 %). Found (%): Pd, 55.33; P, 5.06.  $\text{C}_{172}\text{H}_{324}\text{O}_{28}\text{P}_{12}\text{Pd}_{38}$ . Calculated (%): Pd, 55.73; P, 5.12. IR,  $\nu(\text{CO})/\text{cm}^{-1}$ : 1902 m, 1889 sh, 1852 m, 1845 sh, 1816 w.

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