

## Metal-ligated induced structural interconversion between $\text{Pd}_{23}(\text{CO})_{20}(\text{PEt}_3)_{10}$ and $\text{Pd}_{23}(\text{CO})_{20}(\text{PEt}_3)_8$ possessing highly dissimilar $\text{Pd}_{23}$ core-geometries

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A  $^{31}\text{P}\{^1\text{H}\}$  NMR study has conclusively established that  $\text{Pd}_{23}(\text{CO})_{20}(\text{PEt}_3)_{10}$  (**1**) and  $\text{Pd}_{23}(\text{CO})_{20}(\text{PEt}_3)_8$  (**2**), which differ by only two phosphine ligands, can be chemically induced in solution to interconvert reversibly into each other despite their having highly different metal-core geometries: *viz.*, a centered hexacapped cuboctahedral  $\text{Pd}_{19}$  kernel (pseudo- $O_h$ ) with four wingtip Pd atoms in **1** versus a highly deformed centered hexacapped cubic  $\text{Pd}_{15}$  kernel (pseudo- $D_{2d}$ ) with eight capping Pd atoms in **2**. A structural diagram is given that shows a plausible *hypothetical* pathway for the geometrical transformation of **1** into **2** (or **2** into **1**) upon removal (or addition) of the two phosphine ligands. Although there is no experimental evidence indicating whether these chemically induced conversions are *intermolecular* or *intramolecular*, the proposed *intramolecular* interconversion emphasizes the major structural differences that exist between **1** and **2**. Complete interconversions of **2** into **1** (and **1** into **2**) were accomplished by  $^{31}\text{P}\{^1\text{H}\}$  NMR-monitored reactions carried out within NMR tubes. Addition of “free”  $\text{PEt}_3$  to **2** rapidly converts it into **1**; if an excess of  $\text{PEt}_3$  is added, product **1** slowly transforms into the icosahedral-based  $\text{Pd}_{16}(\text{CO})_{13}(\text{PEt}_3)_9$  (**3**). Addition of  $\text{O}_2$  (air) to **1** converts it into **2** and the phosphine oxide byproduct ( $\text{Et}_3\text{PO}$ ), but the rate of this reverse chemical reaction is not nearly as fast; an excess of  $\text{O}_2$  (air) also slowly converts **3**, if present in the reaction mixture, into **2**; the relatively slow rates of reactions involving **3** are attributed to the icosahedral-based  $\text{Pd}_{16}$  nuclearity in **3** being unlike the identical  $\text{Pd}_{23}$  nuclearities in **1** and **2**. In contrast to the chemically induced interconversion reactions between **1** and **2**, both the reaction of **1** with excess  $\text{PEt}_3$  to form **3** and the reaction of **3** to form **2** are not quantitative. These facile interconversions provide a striking illustration concerning the abnormal capacity of ligated palladium clusters to undergo major changes in metal-core geometries upon addition/removal of ligands. This exceptional behavior may be readily attributed to the markedly weaker M–M and M–CO bonding interactions in palladium carbonyl clusters compared to those in nickel and platinum carbonyl clusters.