INTERCONVERSIONS OF COMPOUNDS OF DIFFERENT NUCLEARITY IN THE $Pd(0)$—CO—PPh_3 SYSTEM

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Mixed-ligand carbonyl—phosphine clusters of palladium and platinum are intermediate between the neutral carbonyl clusters of the metals of the Fe and Co triads [1] and the phosphine clusters of gold [2]. The compounds are distinguished by their increased lability.

The synthesis and interconversions of "Pd_n" clusters with the general formula $Pd_n(CO)_x[P(n\text{-}Alk)_3]_y$, where n = 4 or 10, are known [3-5]. The degree to which the transition from tri-n-alkylphosphine ligands to phosphine ligands with different electronic and steric characteristics, for example, PAr_3 [6], influences the existence of particular structures of the "Pd_n" clusters has remained unclear. In addition, a method for increasing the nuclearity of carbonyl—phosphine clusters of palladium was proposed in [4], and its use in the $Pd(0)$—CO—PAr_3 system seems interesting. As a phosphine ligand we selected PPh_3.

DISCUSSION OF RESULTS

The interconversions studied in the $Pd(0)$—CO—PPh_3 system take place with the participation of the compounds PdL_4 (I), $Pd(CO)L_3$ (II), $Pd_3(CO)_3L_4$ (III), $Pd_4(CO)_5L_4$ (IV), and $Pd_{10}(CO)_{12}L_6$ (V), where L = PPh_3. The "Pd_3" cluster was most often used for the synthesis of the orginal substances, and it was obtained by reducing a water—acetone solution of $Pd(OAc)_2$ by carbon monoxide in the presence of NaOAc with a mole ratio between the orginal reactants $Pd(OAc)_2:L = 1:2$.

The smaller (by four orders of magnitude) basicity of PPh_3 in comparison to $P(n\text{-}Alk)_3$ [7] somewhat limits the choice of reactions which result in an increase in the degree of nuclearity. For this reason, the use of an acid [4] becomes ineffective. The oxidation of PPh_3 by oxygen was found to be convenient. Thus, the treatment of IV-I with a 2:1 O_2—CO mixture gave the decanuclear cluster V:

$$10Pd_4(CO)_5(PPh_3)_4 + 9O_2 \xrightarrow{CO} 4Pd_{10}(CO)_{12}(PPh_3)_6 + 16Ph_3PO + 2CO_2 \tag{1}$$

$$10Pd(PPh_3)_4 + 17O_2 + 12CO \rightarrow Pd_{10}(CO)_{12}(PPh_3)_6 + 34Ph_3PO \tag{2}$$

The formation of the "Pd_{10}" cluster was proved by the set of data from elemental analysis, as well as IR and ^{31}P NMR spectroscopy. The IR spectrum of a solution of cluster V in toluene is characterized by the same set of bands with the same relative intensities as the IR spectrum of a toluene solution of the structurally characterized cluster $Pd_{10}(\mu_2\text{-}CO)_8(\mu_3\text{-}CO)_4(PBu\text{-}n_3)_6$ [8]. The only difference is the displacement of the group of bands in the spectrum of cluster V at 1911, 1895, 1878, 1843, and 1817 cm^{-1} relative to the spectrum of $Pd_{10}(CO)_{12}(PBu\text{-}n_3)_6$ (1892, 1875, 1856, 1828, and 1798 cm^{-1}) by ~20 cm^{-1} toward shorter wavelengths.

The ^{31}P NMR spectrum of the toluene solution at the conclusion of the oxidation of cluster IV points out the formation of Ph_3PO and cluster V. The latter is characterized by two signals at −23.0 and −15.9 ppm with a 2:1 intensity ratio. The difference between the chemical shifts, which equals 7.1 ppm, is the same as in the ^{31}P NMR spectra of the clusters $Pd_{10}(CO)_{12}(PAlk_3)_6$, where Alk = Et, n=Bu [8, 9], $n\text{-}C_8H_{17}$, and $n\text{-}C_{12}H_{25}$ [3]. Thus, the IR and ^{31}P NMR spectra correspond to the structure of a tetracapped octahedron with known coordination of the phosphine ligands at four cap (Pd^7, Pd^8, Pd^9, and Pd^{10}) and two apical (Pd^5 and Pd^6) metal atoms [9] (Fig. 1). The relative intensity of the Ph_3PO and PPh_3 signals (the ratio between them is 1.0:1.6) confirms the stoichiometry of Eq. (1). The amount of CO_2 found at the conclusion of the reaction (1 mmole of CO_2 for every 0.83 mmole of the original "Pd_4") is an indication of the parallel oxidation of CO from the gaseous phase.

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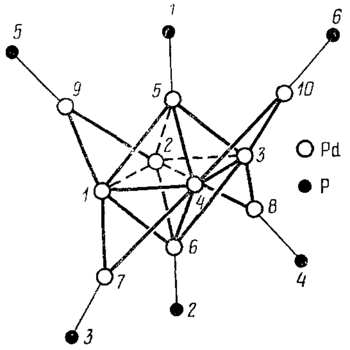


Fig. 1

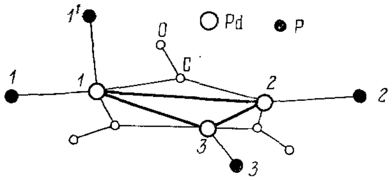


Fig. 2

Fig. 1. Structure of the cluster $Pd_{10}(CO)_{12}(PPh_3)_6$ (V). The CO molecules and phenyl groups are not indicated.

Fig. 2. Structure of the cluster $Pd_4(CO)_5(PPh_3)_4$ (IV). The phenyl groups are not indicated.

Cluster V can trap solvent molecules during crystallization.

The use of an oxidizing agent was unnecessary for increasing the nuclearity of the compounds $Pd_n(CO)_xL_x$, where $n < 4$, in view of the existence of the following equilibria in solution:

$$PdL_4 + CO \rightleftarrows Pd(CO)L_3 + L \tag{3}$$

$$3Pd(CO)L_3 \rightleftarrows Pd_3(CO)_3L_4 + 5L \tag{4}$$

$$4Pd_3(CO)_3L_4 + 3CO \rightleftarrows 3Pd_4(CO)_5L_4 + 4L \tag{5}$$

Equilibria (3) and (4) were reported in [10, 11].

Cluster III is considerably more stable than its analog with $P(n\text{-}Bu)_3$ [4], but III is stable only in the solid state. Cluster III is converted in solution in a CO atmosphere into tetranuclear IV, which was previously characterized as $Pd_3(CO)_3L_3$ [12]. We note that the platinum cluster $Pt_3(CO)_3L_4$ disproportionates under such conditions into $Pt_4(CO)_5L_4$ and $Pt(CO)_2L_2$, where L = PPh_3 [13]. We showed volumetrically that reaction (5) is accompanied by the stoichiometric absorption of CO.

The structures of clusters III and IV (Figs. 2 and 3) were determined by Yu. L. Slovokhotov and Yu. T. Struchkov by x-ray diffraction analysis.

The compositions and yields of the crystallization products of compounds I-III in a CO atmosphere depend on the concentration of the original substances, the solvent, the reaction time, the temperature, and the composition of the gaseous phase. Crystals containing two different clusters can be obtained. For example, the molecular unit $Pd_3(CO)_3(PPh_3)_4 \cdot Pd_4(CO)_5(PPh_3)_4 \cdot C_6H_6$ was revealed by x-ray diffraction analysis.

The "Pd_4" cluster exists in solution in a CO atmosphere in equilibrium with the "Pd_{10}" cluster:

$$5Pd_4(CO)_5L_4 \rightleftarrows 2Pd_{10}(CO)_{12}L_6 + 8L + CO \tag{6}$$

The IR spectrum of a toluene solution of IV in a CO atmosphere displays an absorption band of cluster V at 1911 cm^{-1}. Equilibrium (6) is shifted to the left; therefore, the crystallization of the "Pd_4" cluster from solution in the absence of an agent which binds PPh_3 cannot serve as a method for obtaining the "Pd_{10}" cluster.

Lowering of the nuclearity n is achieved by treating the original compound with free phosphine. Conversions (7) and (8) were realized for the initial ratios "Pd_{10}":L = 1:7 and "Pd_{10}":L = 1:11, respectively:

$$2Pd_{10}(CO)_{12}L_6 + 8L + CO \xrightarrow{\text{toluene}} 5Pd_4(CO)_5L_4 \tag{7}$$

$$3Pd_{10}(CO)_{12}L_6 + 22L \xrightarrow{\text{acetone}} 10Pd_3(CO)_3L_4 + 6CO \tag{8}$$

Cluster III was also obtained from IV in acetone when the initial "Pd_4":L ratio was equal to 1:2.5:

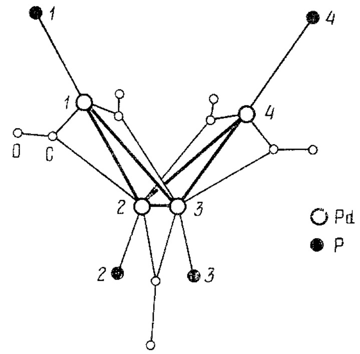


Fig. 3. Structure of the cluster $Pd_3(CO)_3(PPh_3)_4$ (III). The phenyl groups are not indicated.

$$3Pd_4(CO)_5L_4 + 4L \rightarrow 4Pd_3(CO)_3L_4 + 3CO \tag{9}$$

The treatment of any of the clusters "Pd_3," "Pd_4," or "Pd_{10}" with considerable excess of L produces complex I.

Carbonyl—phosphine clusters of Pd also form in disproportionation reactions of compounds with different nuclearity. The interaction of stoichiometric amounts of "Pd_3" and "Pd_{10}" in the presence of L in toluene produces the "Pd_4" cluster:

$$6Pd_3(CO)_3L_4 + Pd_{10}(CO)_{12}L_6 + 5CO \xrightarrow{L} 7Pd_4(CO)_5L_4 + 2L \tag{10}$$

The "Pd_4" cluster was obtained from (V) and (I) in toluene both in the presence of the free phosphine with a mole ratio V:I = 1:1.3 [Eq. (11)] and without the free phosphine with a mole ratio V:I = 1:2 [Eq. (12)]:

$$6Pd_{10}(CO)_{12}L_6 + 8PdL_4 + 13CO \xrightarrow{L} 17Pd_4(CO)_5L_4 \tag{11}$$
$$Pd_{10}(CO)_{12}L_6 + 2PdL_4 + 3CO \rightarrow 3Pd_4(CO)_5L_4 + 2L \tag{12}$$

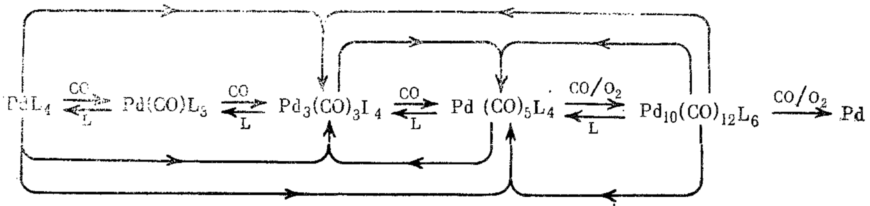
Highly labile cluster III does not form in solution in appreciable amounts even under favorable stoichiometric conditions. The conversion products of V and I in toluene (V:I = 1:4) included only IV and II:

$$Pd_{10}(CO)_{12}L_6 + 4PdL_4 + 5CO \rightarrow 3Pd_4(CO)_5L_4 + 2Pd(CO)L_3 + 4L \tag{13}$$

However, in acetone, in which all the compounds participating in the reactions are poorly soluble, it is possible to obtain III when the V:I mole ratio is equal to 1:5 (14) and when the IV:I mole ratio is equal to 1:2 (15)

$$Pd_{10}(CO)_{12}L_6 + 5PdL_4 + 3CO \rightarrow 5Pd_3(CO)_3L_4 + 6L \tag{14}$$
$$Pd_4(CO)_5L_4 + 2PdL_4 + CO \rightarrow 2Pd_3(CO)_3L_4 + 4L \tag{15}$$

Thus, the general scheme for the interconversions of compounds I-V may be described in the following form:



An important point in Pd(0)—CO—PR_3 systems upon the transition from R = n-Alk to R = Ph is the formation of the "Pd_4" and "Pd_{10}" clusters with the same nuclearity, although PPh_3 differs from $P(n\text{-}Alk)_3$, for example $P(n\text{-}Bu)_3$, with respect to its steric (θ) and electronic (ν) characteristics: $\theta = 145°$ and $\nu = 2068.9\ cm^{-1}$ for PPh_3; $\theta = 132°$ and $\nu = 2060.3\ cm^{-1}$ for $P(n\text{-}Bu)_3$ [6]. Apparently, the formation of tetra- and decanuclear compounds should be expected for other phosphine ligands which are characterized by intermediate values of θ and ν. In particular, $PMePh_2$, $PEtPh_2$, PEt_2Ph, and $P(p\text{-}Tol)_3$ fall in this range [6]. The cluster $Pd_4(CO)_5(PMePh_2)_4$ was obtained with one of these ligands [14].

In the system studied, unlike the system involving $P(n\text{-}Bu)_3$, it is not possible to isolate the second decanuclear cluster with the formula $Pd_{10}(CO)_{14}L_4$ in the individual state. An increase in the time for the treatment of the solutions of clusters IV and V with a mixture of CO and O_2 produces a mixture of $Pd_{10}(CO)_{12}L_6$, $Pd_{10}(CO)_{14}L_4$, and metallic Pd. Another difference is the existence of trinuclear cluster (III) in the solid state.

EXPERIMENTAL

All the operations with carbonyl—phosphine compounds of Pd were carried out in a CO or Ar atmosphere. The compounds were dried in a vacuum over liquid nitrogen. Ultrapure toluene and pure PPh_3 from Chemapol (Czechoslovakia) were dissolved in conc. HCl, filtered, and recrystallized twice after neutralization by NH_4OH from ethanol. The compound PdL_4 was obtained by treating suspensions of the "Pd_{10}" and "Pd_4" clusters in acetone with an excess of L in an Ar atmosphere. The grade of the remaining reagents, their preparation, the method of analysis for CO and CO_2, and the conditions of the volumetric experiment were given in [3, 4, 8]. The analysis for Pd was gravimetric [15]. The samples were mineralized by boiling in a 1:1 $HClO_4$—HNO_3 mixture in the presence of $NaClO_4$. The spectrophotometric method in [16] served as a basis for the analysis for P. The IR spectra were recorded on a Specord-75 IR spectrophotometer with calibration with respect to the absorption band of polystyrene at 1601 cm^{-1}; the accuracy was ±0.5 cm^{-1}. The spectra of solutions were recorded with the use of KBr and CaF_2 cuvettes with thicknesses of 0.127 and 0.139 mm, which were purged with Ar and, in some cases, with CO, after being filled. The selection of the thickness of the reference cuvette made it possible to compensate completely for the absorption bands of benzene and toluene in the region for the vibrations of the CO groups. The remaining IR spectra were recorded with samples suspended in liquid petrolatum. The ^{31}P—$\{^1H\}$ NMR and PMR spectra were recorded on a Bruker SXP4-100 spectrometer in an Ar atmosphere. The positive values in the ^{31}P spectrum correspond to upfield shifts relative to the external reference 85% H_3PO_4.

Synthesis of $Pd(CO)L_3$ from I. A solution of 0.400 g (0.346 mmole) of freshly synthesized I in 10 ml of C_6H_6 was given an addition of a mixture of 10 ml of acetone, 3 ml of AcOH, and 1.5 ml of water. The solution was stirred for 7 h over CO. Crystallization began after the addition of 35 ml of EtOH and 5 ml of water. The pearly crystalline scales were washed with EtOH and pentane. This gave 0.197 g (62%) of II. Found: Pd 11.58; C 71.95; H 5.00; CO 3.42%. $C_{55}H_{45}OP_3Pd$. Calculated: Pd 11.55; C 71.70; H 4.92; CO 3.04%. IR spectrum (νCO, cm^{-1}): 1954 s. The decomposition temperature in a sealed capillary in a CO atmosphere according to the color changes observed above 100°C was: 138°C, to yellowish brown; 150-153°, to dark brown. The decomposition temperature in a sealed capillary in an Ar atmosphere was 50°C, and when Ar was admitted, the pearly color changed to a cream color [10, 11].

Synthesis of $Pd_3(CO)_3L_4$ from II. A solution of 0.400 g (0.434 mmole) of II in 6 ml of C_6H_6 in a CO atmosphere was given an addition of 12 ml of AcOH and, after 3 days of stirring, an addition of 7 ml of EtOH and 4 ml of water. After another 24 h, the bright yellow substance was washed with EtOH. This gave 0.102 g (49%) of III. Found: Pd 21.89; C 61.38; H 4.14%. $C_{75}H_{60}O_3P_4Pd_3$. Calculated: Pd 21.98; C 62.02; H 4.16%. IR spectrum (νCO, cm^{-1}): 1866 s, 1823 vs. Solution in benzene under CO: 2019 w, 1978 s-m, 1965 vs. The decomposition temperature in a sealed capillary in N_2 was $\gtrsim$120°C [11].

Synthesis of $Pd_4(CO)_5L_4 \cdot nC_7H_8$ (n ~ 1) from III. A solution of 2.16 g (1.49 mmole) of III in 110 ml of toluene was given an addition of 220 ml of heptane and left to stand overnight at ~0°C in a CO atmosphere. The dissolution of III in toluene was accompanied by the absorption of 1.06 mmole of CO. The red crystalline substance was washed with heptane. The yield was 1.76 g (95%). Found: Pd 25.30; P 7.31; C 58.85; H 4.66; CO 8.66%. $C_{84}H_{68}O_5P_4Pd_4$. Calculated: Pd 24.93; P 7.26; C 59.11; H 4.02; CO 8.20%. IR spectrum (νCO, cm^{-1}): 1905 vw, 1859 s. Solution in benzene in a CO atmosphere: 1909 w-m, 1867 vs. PMR spectrum (acetone-d_6 relative to TMS; δ, ppm) 7.68-7.27 m (15H, $P[C_6H_5]_3$ and 5H, $CH_3C_6H_5$), 2.40 s (3H, $CH_3C_6H_5$), 2.11 s, (residual protons of acetone-d_6). The synthesis is similar to the synthesis of "$Pd_3(CO)_3L_3$" from $Pd_3(CO)_3L_4$ [12].

Synthesis of $Pd_{10}(CO)_{12}L_6$ from $Pd_4(CO)_5L_4 \cdot nC_7H_8$ (n ~ 1). A 1.42-g portion (0.83 mmole) of $Pd_4(CO)_5L_4 \cdot nC_7H_8$ (n ~ 1) was dissolved in 45 ml of toluene in a CO atmosphere, and the solution was stirred for 1 h in a 2:1 O_2—CO atmosphere. The gaseous phase was removed by carbon monoxide and passed through a solution of $Ba(OH)_2$; 1.0 mmole of CO_2 was found. According to the TLC data on Silufol, the solution contains PhPO: R_f 0.13 (the front reached 81 mm, and the eluent was Et_2O), which is identical to the chromatogram of the pure Ph_3PO used as a reference. The solution was filtered to remove the small quantity of metallic Pd, 80 ml of pentane were added, and the mixture was held for 3 h at ~0°C. The dark red substance was washed with EtOH, a small quantity of acetone, and pentane and dried for 15 min. The substance darkens in a vacuum, but it takes on the original color when CO is admitted. This gives 0.86 g (87%) of V. Found: Pd 35.36; P 6.17; C 48.41; H 3.15%. $C_{120}H_{90}O_{12}P_6Pd_{10}$. Calculated: Pd 35.78; P 6.25; C 48.47; H 3.05%. IR spectrum in a benzene solution in a CO atmosphere (νCO, cm^{-1}): 1910 s, 1894 m, 1877 s, 1843 w. $^{31}P-\{^1H\}$ NMR spectrum at the conclusion of the reaction (toluene, δ, ppm): −23.7 (Ph_3PO) (a), −23.0 (b), −15.9 (c) with the intensity ratios a:(b + c) = 1.0:1.6 and b:c = 1.9:1.0.

Synthesis of $Pd_{10}(CO)_{12}L_6$ from III. A 0.900-g portion (0.62 mmole) of III was dissolved in 33 ml of toluene under CO. After 1.5 h of stirring in a 2:1 O_2—CO atmosphere, the dark red solution was filtered to remove the small quantity of metal, 20 ml of heptane were added, and the mixture was left to stand at ~0°C. The dark red crystalline substance was washed with EtOH and heptane. This gave 0.392 g (71%) of V. Found: Pd 35.17; P 6.21; C 48.66; H 3.15%. The IR spectrum of the benzene solution was identical to the IR spectrum of the product of the preceding synthesis.

Synthesis of $Pd_{10}(CO)_{12}L_6$ from I. A 2.24-g portion (1.94 mmole) of I was dissolved in 30 ml of toluene under CO. The solution was stirred for 1.5 h in a 2:1 O_2—CO atmosphere and then for an additional 2 h under CO. After 68 min of stirring in a 2:1 O_2—CO mixture, the IR spectrum of the solution had only vibrational bands for cluster V (νCO, cm^{-1}): 2045 w, 1971 br, w, 1912 s, 1896 w, 1879 s, 1843 w, 1818 m. The solution was filtered, the solvent was removed in a vacuum, and 20 ml of EtOH were added. The substance was washed with EtOH and ether. This gave 0.496 g (86%) of V. Found: Pd 35.73; P 6.11%. IR spectrum (νCO, cm^{-1}): 2039 w, 1906 s, 1891 s, 1871 s, 1840 sh, 1809 m.

Synthesis of $Pd_4(CO)_5L_4 \cdot nC_7H_8$ (n ~ 1) from V. A solution of 0.193 g (0.065 mmole) of V in 12 ml of toluene was given an addition of 0.125 g (0.477 mmole) of L with stirring. After 4 h of stirring under CO, 30 ml of heptane were added, and the mixture was left to stand for 24 h at ~0°C. This gave 0.196 g (70%). IR spectrum (νCO, cm^{-1}): 1904 w, 1858 s.

Synthesis of $Pd_3(CO)_3L_4$ from V. A suspension of 0.200 g (0.067 mmole) of V in 10 ml of acetone was given an addition of 0.197 g (0.75 mmole) of L. After 3 days of stirring under CO, 1 ml of water was added, and after an additional 5 h of stirring, the yellow substance was washed with EtOH containing ~1% AcOH. This gave 0.270 g (83%) of III. Found: Pd 22.40; P 8.30%. $C_{75}H_{60}O_3P_4Pd_3$. Calculated: Pd 21.98; P 8.53%. IR spectrum (νCO, cm^{-1}): 1905 w, 1891 w, 1863 s-m, 1816 s, 1790 sh.

Synthesis of $Pd_3(CO)_3L_4$ from $Pd(CO)_5L_4 \cdot nC_7H_8$ (n ~ 1). A solution of 0.300 g (0.176 mmole) of $Pd_4(CO)_5L_4 \cdot nC_7H_8$ (n ~ 1) in 15 ml of acetone under CO was given an addition of 0.115 g (0.439 mmole) of L. The experiment was subsequently carried out in analogy to the preceding synthesis. This gave 0.280 g (82%) of III. The IR spectrum of the product was identical to the IR spectrum of III.

Synthesis of $Pd_4(CO)_5L_4 \cdot nC_7H_8$ (n ~ 1) from V and III. A solution of 0.102 g (0.034 mmole) of V in 14 ml of toluene was given an addition of 0.300 g (0.207 mmole) of III and 0.066 g (0.252 mmole) of L. After 1.5 h of stirring under CO, the solution was filtered, given an addition of 30 ml of hexane, and left to stand for 24 h at −10°C. The yield was 0.373 g (90%). The IR spectrum of the product was identical to the IR spectrum of $Pd_4(CO)_5L_4 \cdot nC_7H_8$ (n ~ 1).

Synthesis of $Pd_4(CO)_5L_4 \cdot nC_7H_8$ and II from V and I and Synthesis of IV from V and I. A solution of 0.172 g (0.058 mmole) of V in 15 ml of toluene was given an addition of 0.400 g (0.347 mmole) of I. After 1 h of stirring under CO, an additional 0.085 g (0.029 mmole) of V was added. After 3 h of stirring, the solution was filtered, 30 ml of hexane were added, and the mixture was left to stand at −10°C. This gave 0.457 g of a mixture of red crystals of $Pd_4(CO)_5L_4 \cdot nC_7H_8$ (n ~ 1) and pearly crystals of II. IR spectrum (νCO, cm^{-1}): 1954 s, 1859 s.

A solution of 0.358 g (0.120 mmole) of V in 20 ml of toluene was given an addition of 0.277 g (0.240 mmole) of I. After 24 h of stirring under CO, the solution was filtered, and 40 ml of hexane were added. This gave 0.505 g (86%) of IV. Found: Pd 26.16; P 7.65%. $C_{77}H_{60}O_5P_4Pd_4$. Calculated: Pd 26.36; P 7.67%. IR spectrum (νCO, cm^{-1}): 1957 br, s.

A solution of 0.200 g (0.067 mmole) of V in 15 ml of toluene was given an addition of 0.103 g (0.089 mmole) of I and 0.066 g (0.252 mmole) of L and stirred in a CO atmosphere for 1.5 h. The yield was 0.256 g (79%). The IR spectrum of the product was identical to the IR spectrum of $Pd_4(CO)_5L_4 \cdot nC_7H_8$ (n ~ 1).

Synthesis of $Pd_3(CO)_3L_4$ from $Pd_4(CO)_5L_4 \cdot nC_7H_8$ (n ~ 1) and I. A suspension of 0.199 g (0.117 mmole) of $Pd_4(CO)_5L_4 \cdot nC_7H_8$ (n ~ 1) and 0.270 g (0.234 mmole) of I in 11 ml of acetone was stirred for 24 h under CO. The yellow precipitate was washed with EtOH containing ~1%

AcOH. This gave 0.285 g (84%) of III. Found: Pd 22.07; P 8.49%. The IR spectrum of the product was identical to the IR spectrum of III.

Synthesis of $Pd_3(CO)_3L_4$ from V and I. A suspension of 0.200 g (0.067 mmole) of V and 0.388 g (0.336 mmole) of I in 16 ml of acetone was stirred for 24 h under CO. This gave 0.360 g (74%) of III. Found: Pd 22.28; P 8.46%. The IR spectrum of the product was identical to the IR spectrum of III.

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CONCLUSIONS

1. Interconversions of mono-, tri-, tetra-, and decanuclear palladium compounds take place in the zerovalent-palladium—carbon monoxide—triphenylphosphine system.

2. An increase in the nuclearity to 10 is achieved by oxidizing the phosphine ligand; a decrease in nuclearity is produced by treating the compounds with the appropriate amount of free triphenylphosphine.

3. The reactions provide a convenient method for the synthesis of tri-, tetra-, and decanuclear carbonyl—triphenylphosphine clusters of Pd(0).

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