

SYNTHESIS AND PROPERTIES OF STABLE PALLADIUM(0) CARBONYL COMPLEXES CONTAINING TRIPHENYLPHOSPHINE

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SUMMARY

The synthesis and properties of the stable zerovalent palladium carbonyl complexes are described. Mononuclear $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ has been prepared in good yield by two different routes i.e., the reaction of palladium(II) acetylacetonate with triethylaluminum and the reaction of dichloro-bis(triphenylphosphine)palladium(II) with sodium borohydride, both in the presence of triphenylphosphine under carbon monoxide. The trinuclear cluster $[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_3]$ has been obtained by the reaction between equimolar quantities of palladium(II) acetylacetonate and triphenylphosphine. Another trinuclear cluster complex $[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_4]$ has been prepared by heating $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ in ether, an equilibrium between these two complexes being observed in solution. Oxidative addition reactions of $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ with methyl iodide, allyl chloride, and vinyl chloride gave the corresponding acyl complexes of the type *trans*- $\text{PdX}(\text{COR})(\text{PPh}_3)_2$.

INTRODUCTION

Although the simple binary palladium carbonyl $[\text{Pd}(\text{CO})_n]$ is unknown, several carbonyl halides of the type $[\text{PdX}_2(\text{CO})]_n$ (ref. 1), $[\text{PdX}_3(\text{CO})]^-$ (ref. 2), or $[\text{Pd}_2\text{Cl}(\text{CO})_2]_n$ (ref. 3), and the phosphine-substituted carbonyl complex *trans*- $[\text{PdCl}(\text{CO})(\text{PEt}_3)_2][\text{BF}_4]$ (ref. 4) have been prepared. Recently the preparation of a zerovalent palladium carbonyl complex, which is too unstable to be isolated but estimated as $\text{Pd}(\text{CO})(\text{PF}_3)(\text{PPh}_3)_2$, has been reported⁵. All these carbonyl complexes are very unstable and no characterization has been described, in contrast to the situation with nickel or platinum carbonyl complexes. As reported in a previous communication⁶, however, we have succeeded in isolating the zerovalent palladium carbonyl complexes stabilized with triphenylphosphine, i.e. $\text{Pd}(\text{CO})(\text{PPh}_3)_3$, $[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_3]$, and $[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_4]$, these being the first stable carbonyl complexes of palladium reported. In this paper we describe the preparation and properties of these complexes in more detail.

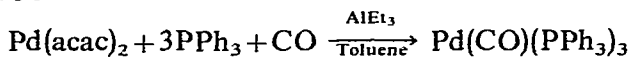
RESULTS AND DISCUSSION

Preparation of $\text{Pd}(\text{CO})(\text{PPh}_3)_3$

The mononuclear complex $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ can be prepared by two different

routes, (A): the reduction of palladium(II) acetylacetonate with triethylaluminum as previously reported⁶, and (B) the reduction of $\text{PdCl}_2(\text{PPh}_3)_2$ with sodium borohydride, both in the presence of triphenylphosphine under carbon monoxide.

Method A. When carbon monoxide was bubbled through a toluene solution containing palladium(II) acetylacetonate (1 mole), triphenylphosphine (3 mole), and triethylaluminum at temperatures within the range -50° to 10° , the original dark red color of the solution lightened and $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ was precipitated in 70–80% yield.

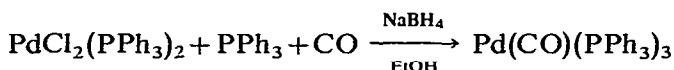


In the absence of carbon monoxide, $\text{Pd}(\text{PPh}_3)_4$ and metallic palladium were produced.

When two moles of triphenylphosphine were used with the same quantity of palladium(II) acetylacetonate, the dicarbonyl complex $\text{Pd}(\text{CO})_2(\text{PPh}_3)_2$ was not obtained, the main product being apparently $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ together with small quantities of $[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_3]$ and $[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_4]$.

$\text{Pd}(\text{PPh}_3)_4$ dissociates to $\text{Pd}(\text{PPh}_3)_3$ in solution⁷, and for this reason the reaction of $\text{Pd}(\text{PPh}_3)_4$ with carbon monoxide was examined as a method of preparing $\text{Pd}(\text{CO})(\text{PPh}_3)_3$. The latter compound, however, was not obtained when carbon monoxide was bubbled through a solution of $\text{Pd}(\text{PPh}_3)_4$ in benzene at room temperature. Addition of triphenylphosphine to a solution of $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ caused the immediate evolution of carbon monoxide and led to the formation of $\text{Pd}(\text{PPh}_3)_4$, thus demonstrating the strong coordination tendencies of triphenylphosphine towards coordinatively unsaturated $\text{Pd}(\text{PPh}_3)_3$.

Method B. $\text{Pd}(\text{PPh}_3)_4$ may be produced by the reduction of $\text{PdCl}_2(\text{PPh}_3)_2$ with sodium borohydride in the presence of excess triphenylphosphine, under an atmosphere of nitrogen. $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ may be obtained from a similar reaction if a mixture of $\text{PdCl}_2(\text{PPh}_3)_2$ and triphenylphosphine, in the molar ratio of triphenylphosphine/Pd of 3/1, is allowed to react under an atmosphere of carbon monoxide. The synthesis may be represented by the following equation:

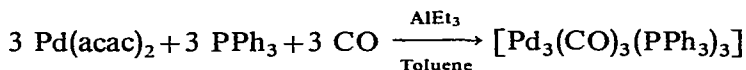


Thus, sodium borohydride was added to a suspension of $\text{PdCl}_2(\text{PPh}_3)_2$ (1 mole) and triphenylphosphine (1 mole) at -45° , carbon monoxide immediately introduced and the temperature allowed to rise gradually to room temperature. The original yellow color of the suspension turned to pale yellow as the reaction proceeded, and $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ was obtained in 80–90% yield.

Although both methods give good yield, Method B is the more attractive in that it employs sodium borohydride as a reducing agent, rather than the more dangerous reagent triethylaluminum used in Method A.

Preparation of $[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_3]$

The red cluster carbonyl $[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_3]$ was obtained directly in high yield by a similar reaction to Method A used for the preparation of $\text{Pd}(\text{CO})(\text{PPh}_3)_3$, using equimolar quantities of triphenylphosphine and palladium(II) acetylacetonate.



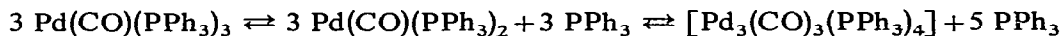
Preparation of $[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_4]$

As described in a preliminary report⁶, $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ loses triphenylphosphine in solution, giving the orange-yellow cluster compound $[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_4]$. The quantitative preparation of this trinuclear complex was achieved by refluxing an ether suspension of $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ under carbon monoxide. If methanol is employed as a solvent instead of ether, then prolonged heating of the reaction mixture is necessary to achieve the same result.

Properties of the carbonyl complexes

All the three carbonyl complexes are stable in an inert atmosphere but slowly decompose in air. In solution they decompose rapidly when exposed to air. They react with excess triphenylphosphine, losing carbon monoxide and converting into $\text{Pd}(\text{PPh}_3)_4$.

Despite the low solubilities of these complexes, their molecular weights were carefully re-examined using a cryoscopic method, and the evidence for the trinuclear structure of $[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_3]$ was obtained. The complex $[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_4]$ appears to be largely dissociated in benzene, and as the data for $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ also indicate a very low molecular weight it is suggested that $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ loses triphenylphosphine in solution to yield the coordinatively unsaturated species $\text{Pd}(\text{CO})(\text{PPh}_3)_2$. Thus, in solution, the following equilibria exist between $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ and $[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_4]$:



The above equilibria shift to the left-hand side of the equation at low temperature as indicated by the fact that the addition of stoichiometric amounts of triphenylphosphine to $[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_4]$ in ether below -20° led to the conversion of the cluster complex to $\text{Pd}(\text{CO})(\text{PPh}_3)_3$. Since $[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_4]$ and $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ are respectively orange-yellow and cream-yellow in color, transformation of the former to the latter and *vice versa*, is easily followed visually. At room temperature the above equilibria lie to the right-hand side of the equation and for this reason any purification of $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ must be carried out carefully at low temperature in order to avoid transformation to the trinuclear complex. The unsaturated compound $\text{Pd}(\text{CO})(\text{PPh}_3)_2$ easily interacts with an attacking species, *e.g.* with alkyl halides it gives acyl complexes of the type *trans*- $\text{PdX}(\text{COR})(\text{PPh}_3)_2$, and with excess triphenylphosphine it loses carbon monoxide and is converted into $\text{Pd}(\text{PPh}_3)_4$.

The infrared spectrum of $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ shows a strong absorption at 1955 cm^{-1} assignable to the terminal carbonyl stretching vibration, which is lower than the reported value (2018 cm^{-1}) for $\text{Pd}(\text{CO})(\text{PF}_3)(\text{PPh}_3)_2$ which as mentioned above is too unstable to be isolated⁵. The appreciable stability of $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ is demonstrated by the fact that in the crystalline state the complex remains unchanged in air for several hours. Substitution of trifluorophosphine in $\text{Pd}(\text{CO})(\text{PF}_3)(\text{PPh}_3)_2$ with the more basic triphenylphosphine causes a higher electron density at the metal atom in $\text{Pd}(\text{CO})(\text{PPh}_3)_3$, thus increasing the back-donation to the carbonyl ligand which, in turn, leads to the increased stabilization of the palladium-carbon bond and a shift

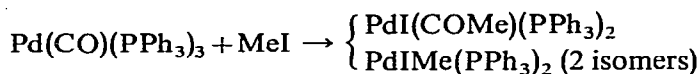
in the carbonyl stretching frequency of the compound to lower values.

The infrared spectra of the cluster complexes exhibit only bridging carbonyl vibrations between 2000 and 1700 cm^{-1} . The red cluster compound $[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_3]$ has only one absorption band at 1850 cm^{-1} which is consistent with a D_{3h} structure for the trinuclear complex similar to that in the analogous platinum complex $[\text{Pt}_3(\text{CO})_3(\text{PPh}_2\text{PhCH}_2)_3]^8$. The orange-yellow cluster compound $[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_4]$ has two absorption bands at 1845 and 1820 cm^{-1} which are consistent with a C_{2v} structure which, from symmetry considerations, is similar to that of $[\text{Pt}_3(\text{CO})_3(\text{PPh}_3)_4]^8$. From this evidence it is therefore reasonable to exclude the possibility, that the tri-nuclear cluster $[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_4]$ may be a tetranuclear complex such as $[\text{Pt}_4(\text{CO})_5(\text{PPh}_3)_4]^8$.

Reactions of $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ with alkyl halides

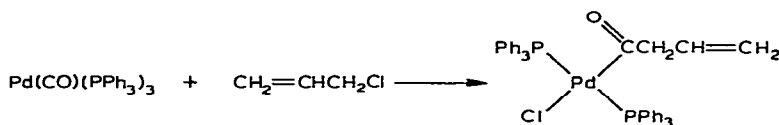
The oxidative addition reactions of $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ with methyl iodide, allyl chloride, and vinyl chloride have been investigated. In all cases reaction proceeded rapidly, yielding corresponding acyl complexes of the type *trans*- $\text{PdX}(\text{COR})(\text{PPh}_3)_2$.

The reaction with methyl iodide was studied in the presence of a nitrogen or carbon monoxide atmosphere, and gave acetyl and methyl complexes in variable ratio. When methyl iodide was added to a toluene solution of $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ a pink methyl complex was precipitated. This was separated by filtration, and orange acetyl and yellow methyl complexes obtained after addition of n-hexane to the filtrate.



The acetyl complex showed a strong absorption at 1690 cm^{-1} , assignable to $\nu(\text{C}=\text{O})$.

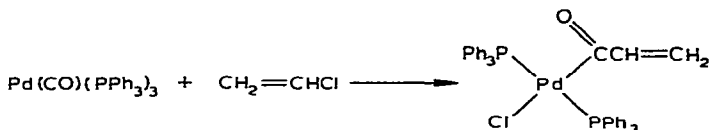
Allyl chloride reacted with $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ to give the white to pale-yellow 3-butenyl complex



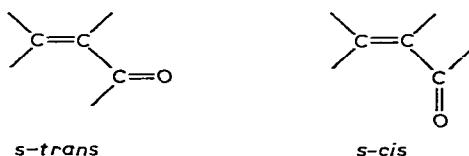
The infrared spectrum of this complex exhibited absorptions at 1675, 1636 and 320 cm^{-1} , assignable to $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{C})$ and $\nu(\text{Pd}-\text{Cl})$ respectively. The presence of $\nu(\text{Pd}-\text{Cl})$ indicates that the complex has a *trans* structure, with the chlorine *cis* to the phosphine ligands. If the chlorine were *trans* to the phosphine ligands, then $\nu(\text{Pd}-\text{Cl})$ would be expected to occur in the 290–270 cm^{-1} region of the spectrum due to the strong *trans* effect of the phosphine ligands. Deformations of terminal vinyl group occur at 990 and 905 cm^{-1} .

In contrast to the other alkyl halides studied, vinyl chloride is less reactive towards $\text{Pd}(\text{CO})(\text{PPh}_3)_3$. When vinyl chloride was bubbled for two hours at room temperature through a toluene solution of $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ the complex isolated was $\text{Pd}(\text{PPh}_3)_4$. The oxidative addition product was however obtained if bubbling of vinyl chloride was discontinued after a short time interval.

The yellow complex has a strong absorption band in its infrared region at 1665 cm^{-1} assignable to $\nu(\text{C}=\text{O})$, and a weak band at 1620 cm^{-1} assignable to $\nu(\text{C}=\text{C})$. Ac-



According to Bellamy, conjugation effects in α,β -unsaturated ketones are such that in the *s-trans* compounds the separation of the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ bands is usually less than 60 cm^{-1} , whereas in the *s-cis* compounds a greater separation occurs. In addition, in the *s-trans* compounds the carbonyl bands are always much stronger than the $\text{C}=\text{C}$ absorptions, whereas in the *s-cis* series the olefinic bands are much stronger than in the *s-trans* series. These effects have been ascribed to a greater degree of vibrational coupling between the two bands⁹.



In the complex obtained in this study it is reasonable to assume the occurrence of an *s-trans* configuration since the separation of the two bands is 45 cm^{-1} and the $\text{C}=\text{O}$ band is much stronger than the $\text{C}=\text{C}$ band.

EXPERIMENTAL

All procedures were carried out in an atmosphere from which oxygen was rigorously excluded. Carbonyl and acyl complexes were stored under carbon monoxide. Infrared spectra were recorded (as KBr disks or Nujol mulls) on Japan Spectroscopic DS-301 and DS-403G spectrophotometers. Melting points were determined in an argon atmosphere and are recorded uncorrected.

Carbonyl-tris(triphenylphosphine)palladium(0), $\text{Pd}(\text{CO})(\text{PPh}_3)_3$

Method A. When carbon monoxide was bubbled through a toluene solution (40 ml) containing palladium(II) acetylacetonate (2.25 g), triphenylphosphine (5.79 g), and triethylaluminum (1.0 ml) for 3 h at -50° to 10° , $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ was precipitated as a cream-yellow solid. The complex was collected by filtration, washed with *n*-hexane and ether under carbon monoxide below -20° and dried *in vacuo*. A yield of 5.3 g (78%) of $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ was obtained, decomp. 110° . (Found: C, 71.46; H, 5.13; Pd, 11.6. $\text{C}_{55}\text{H}_{45}\text{O}\text{P}_3\text{Pd}$ calcd.: C, 71.70; H, 4.93; Pd, 11.55%.)

Method B. To a suspension of $\text{PdCl}_2(\text{PPh}_3)_2$ (0.35 g) and triphenylphosphine (0.14 g) in ethanol (15 ml), sodium borohydride (0.12 g) was added at -45° , and carbon monoxide immediately bubbled through the solution. The temperature was allowed to rise to room temperature gradually over a period of 4 h, and the reaction continued for another 2 h at room temperature. As the reduction proceeded, the original yellow color of the suspension paled and $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ was obtained as a cream-yellow precipitate. The complex was washed with ethanol/water (1/1) and ethanol repeatedly, and dried. A yield of 0.4 g (87%) of $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ was obtained.

Tri-μ-carbonyl-tris(triphenylphosphine)tripalladium(0), [Pd₃(CO)₃(PPh₃)₃]

This cluster carbonyl was prepared by a similar reaction to that used in *Method A* for the preparation of Pd(CO)(PPh₃)₃. In this case carbon monoxide was bubbled for 3 h through a solution of palladium(II) acetylacetonate (0.46 g), triphenylphosphine (0.41 g), and triethylaluminum (0.2 ml) in toluene (10 ml). After addition of n-hexane (4 ml) to the reaction solution at -10°; red crystals were obtained and after working-up the solution 0.55 g (93%) of [Pd₃(CO)₃(PPh₃)₃] was isolated; decomp. 73°. (Found: C, 57.11; H, 4.17; Pd, 26.3; mol.wt., 1040. C₅₇H₄₅O₃P₃Pd₃ calcd.: C, 57.53; H, 3.82; Pd, 26.82%; mol.wt., 1190.)

Tri-μ-carbonyl-tetrakis(triphenylphosphine)tripalladium(0), [Pd₃(CO)₃(PPh₃)₄]

When Pd(CO)(PPh₃)₃ (0.23 g) was refluxed in ether (10 ml) under carbon monoxide the color of the suspension turned from cream-yellow to orange-yellow, transformation to the trinuclear complex being completed after 30 min. The cluster complex was washed repeatedly with ether and dried to give 0.11 g (93%) of [Pd₃(CO)₃(PPh₃)₄], decomp. 70°. (Found: C, 61.64; H, 4.28; Pd, 23.2 C₇₅H₆₀O₃P₄Pd₃ calcd.: C, 62.00; H, 4.17; Pd, 21.97%.)

Oxidative addition reactions of Pd(CO)(PPh₃)₃

Reaction with methyl iodide. Pd(CO)(PPh₃)₃ (0.14 g) was treated with methyl iodide (0.05 ml) in toluene (10 ml) at -40°. PdIme(PPh₃)₂ separated as a pink precipitate (0.01 g, 6.5%), and after addition of n-hexane to the filtrate PdI(COMe)(PPh₃)₂ was isolated as orange-red crystals (0.039 g, 26%) and PdIme(PPh₃)₂ as yellow crystals (0.035 g, 23%). PdI(COMe)(PPh₃)₂, decomp. 141° (Found: C, 57.18; H, 4.06. C₃₈H₃₃IOP₂Pd calcd.: C, 57.00; H, 4.13%). PdIme(PPh₃)₂ (pink isomer), decomp. 168° (Found: C, 56.98; H, 4.31. C₃₇H₃₃IP₂Pd calcd.: C, 57.49; H, 4.31%). PdIme(PPh₃)₂ (yellow isomer), decomp. 130° (Found: C, 57.39; H, 3.80%).

Reaction with allyl chloride. Pd(CO)(PPh₃)₃ (0.15 g) was treated with 0.3 ml of allyl chloride in toluene (10 ml) at room temperature, and after an hour n-hexane was added. *trans*-PdCl(COCH₂CHCH₂)(PPh₃)₂ separated as white to pale yellow needles (0.11 g, 82%), decomp. 115° (turning yellow above 65°). Found: C, 65.20; H, 5.19; Cl, 5.00. C₄₀H₃₅ClOP₂Pd calcd.: C, 65.32; H, 4.75; Cl, 4.82%.)

Reaction with vinyl chloride. Vinyl chloride was bubbled through a toluene solution (7 ml) containing 0.11 g of Pd(CO)(PPh₃)₃ for 3 min at room temperature and n-hexane was added to the solution. After cooling at -78°, Pd(PPh₃)₄ (0.05 g) precipitated and was filtered off. From the filtrate 0.01 g (12%) of *trans*-PdCl(COCHCH₂)(PPh₃)₂ was obtained as orange-yellow crystals. (Found: C, 64.31; H, 4.80. C₃₉H₃₃ClOP₂Pd calcd.: C, 64.92; H, 4.61%.)

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