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# Chemistry of Platinum Hydrides. Part XXII. Formation of Trinuclear Cluster Complexes from Platinum(II) Dihydrides Containing Bulky Phosphines

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*Carbon monoxide reacts readily under ambient conditions with platinum(II) dihydrides containing bulky phosphines, $PtH_2(PR_3)_2$ (where $PR_3$ = $Cy_3P$, $Pr^i_3P$, $Bu^t_2Bu^nP$ and $Bu^tPh_2P$) in benzene solution displacing hydrogen as well as one phosphine ligand and giving trinuclear cluster complexes containing bridging carbonyl groups. These cluster complexes, which can also be prepared by the reactions of carbon monoxide with $(PR_3)_2Pt$, undergo oxidative addition reactions with iodine, giving tetracoordinated platinum(II) complexes, $PtI_2(PR_3)(CO)$.*

## Introduction

Donor ligands such as carbon monoxide, tertiary phosphines, arsines, pyridine, *etc.* displace hydrogen from transition metal hydrides [1]. For platinum hydrides, there has been only a brief report [2] without experimental details, of the conversion, by reaction with carbon monoxide of *trans*-$PtH_2[P(C_6H_{11})_3]_2$ to give $Pt_3(CO)_3L_3$ and $Pt_3(CO)_3L_4$ (L = tricyclohexylphosphine), the crystal structures of both of which have been determined [2, 3]. This contrasts with the reaction of *trans*-$PdClCH_3(PMe_2Ph)_2$ with carbon monoxide in which insertion of CO into the palladium–alkyl bond occurs [4]. Recently, we have developed a general and convenient preparative route to several stable platinum(II) dihydrides [5], and we now describe the sequence of reactions whereby these dihydrides are converted, by reduction with carbon monoxide, to the trinuclear complex.

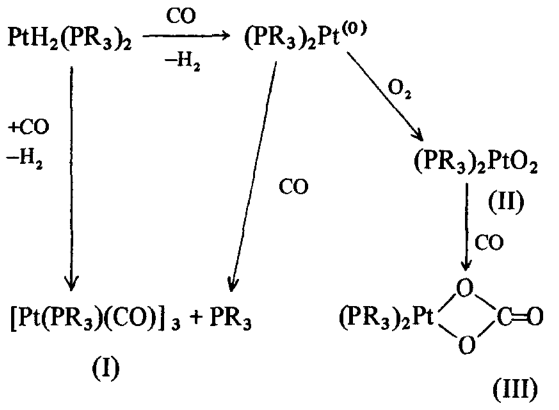
When a stream of oxygen-free carbon monoxide is passed slowly through a benzene solution of any of the platinum(II) dihydrides, $PtH_2(PR_3)_2$ ($PR_3$ = $Cy_3P$, $Pr^i_3P$, $Ph_2Bu^tP$, $Bu^t_2Bu^nP$), under nitrogen, a red solution results within one minute accompanied by the evolution of hydrogen gas. The $^{31}P$ nmr spectrum of this red solution showed a very broad resonance at 19.8 ppm. This is indicative of a rapid equilibrium occurring in the solution presumably between species such as $[Pt(PR_3)(CO)]_3$ and $Pt_3(PR_3)_4(CO)_3$. Addition of alcohol to a concentrated solution produces orange-red crystals. The remaining solution contains a mol of phosphine per mol of $PtH_2(PR_3)_2$ as characterized by its $^1H$ nmr spectra. The crystals, identified as $[Pt(PR_3)(CO)]_3$ (I), retain benzene solvent very tightly even under reduced pressure.

The infrared spectrum of this trinuclear complex shows a strong band in the region 1750–70 $cm^{-1}$ due to the bridging carbonyl group [6]. The $^{31}P$ nmr spectrum of $Pt_3(PCy_3)_3(CO)_3$ in $CDCl_3$ was well-resolved and consisted of a sharp singlet at 67.1 ppm flanked on either side by doublet satellites of approximately one-quarter intensity centred at 58.6 and 75.5 ppm. This entire pattern had further complex satellites centred at about –25.8 and 160.2 ppm each consisting of at least 5 resonances.

When the above reaction is carried out for 10 minutes in an open flask exposed to air, the same complex (I) along with both dioxygen platinum(II) complexes [5, 7] and platinum(II) carbonato [5, 8] complexes is formed. The formation of the dioxygen complex, $(PR_3)_2PtO_2$, (II), is indicated by the presence of a strong infrared absorption in the region 817–26 $cm^{-1}$ due to $\nu(PtO_2)$ while a band at ~1680 $cm^{-1}$ suggests the presence of $(PR_3)_2PtCO_3$, (III). Further passage of CO for ~2h to the solution of this mixture causes an increase in the intensity of the carbonato band at ~1680 $cm^{-1}$ and the disappearance of the dioxygen band in the region 817–26 $cm^{-1}$. Evidently, the dioxygen complex (II) is converted to the carbonato-complex (III) [5, 8].

These observations suggest that the conversion of $PtH_2(PR_3)_2$ to trinuclear cluster complexes involves, firstly, reduction to the zerovalent bis(trialkylphosphine)platinum, and, secondly, displacement of one phosphine ligand by carbon monoxide to produce the bridging trinuclear cluster complex (I). In the presence of oxygen, the bis(trialkylphosphine)platinum(0) complexes which are known to be very oxygen sensitive, readily give the dioxygen platinum(II) complexes [5, 7].

The reaction of carbon monoxide with this dioxygen platinum(II) complex is quite slow, requiring about 2 to 3 hr for completion [5, 9]. Hence, the dioxygen complex is observed as a product whenever oxygen is present during the reaction.



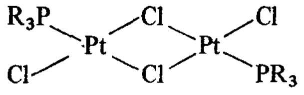
(1)

The above reaction sequence for the reaction of carbon monoxide with $PtH_2(PR_3)_2$ is further supported by the fact that when carbon monoxide is allowed to react with $(PR_3)_2Pt^{(0)}$ (II), in the absence of oxygen, the same trinuclear complex (I) is obtained in almost quantitative yield, with displacement of one equivalent of free phosphine. A similar trinuclear complex containing the less bulky triphenylphosphine has been prepared previously by the reaction of carbon monoxide with $(Ph_3P)_4Pt^{(0)}$ under high pressure and temperature [6], while Otsuka and coworker [10] have very recently prepared some similar complexes of palladium and one complex of platinum by the same method.

These trinuclear cluster complexes (I) react readily with iodine in benzene solution cleaving the carbonyl bridge to give platinum(II) iodide complexes (IV) containing phosphine and terminal carbonyl ligands (eq. 2).

$$[Pt(PR_3)(CO)]_3 + 3I_2 \longrightarrow \underset{(IV)}{3PtI_2(PR_3)(CO)} \quad (2)$$

These complexes give strong bands due to terminal carbonyl groups at (range) 2075–2085 $cm^{-1}$. Similar complexes can also be prepared as reported by Wallbridge *et al.* [11] *i.e.* by the reaction of carbon monoxide with chlorine bridged complex



## Acknowledgments

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