

Preliminary communication

Stable palladium(0) carbonyl complexes

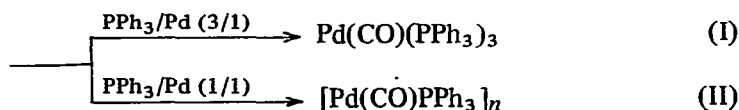
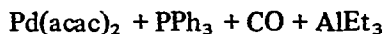
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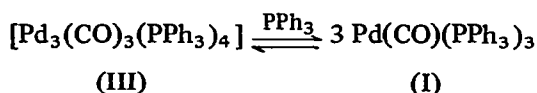
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There have been many reports on carbonyl complexes of nickel(0) and platinum(0). But as for palladium, only one zero valent carbonyl complex, which was not isolated, has been reported¹. In course of studies on transition metal complexes containing small covalent molecules, *e.g.* nitrogen², hydrogen³, carbon monoxide⁴, etc., we have found stable palladium(0) carbonyl complexes with tertiary phosphines.

When carbon monoxide was bubbled through a toluene solution containing palladium(II) acetylacetonate (1 mole), triphenylphosphine (3 moles), and triethylaluminum at -50 to 10° , the original dark red colour of the solution changed to red and after several hours a cream-yellow $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ (I) precipitated. In the case of the reaction using equimolar palladium(II) acetylacetonate and triphenylphosphine, red crystals of $[\text{Pd}(\text{CO})\text{PPh}_3]_n$ (II) were obtained by adding *n*-hexane to the reaction solution. In solution $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ loses triphenylphosphine, giving an orange-yellow



$[\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_4]$ (III) at room temperature, and between (I) and (III) the following equilibrium is observed.



The reactions of these complexes with a large excess of triphenylphosphine gave the known complex $\text{Pd}(\text{PPh}_3)_4$, but $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ could not be obtained by the reaction of $\text{Pd}(\text{PPh}_3)_4$ with carbon monoxide, although the reaction of $\text{Pt}(\text{PPh}_3)_4$ with carbon monoxide yields carbonyl complexes, $\text{Pt}(\text{CO})_2(\text{PPh}_3)_2$ and $\text{Pt}(\text{CO})(\text{PPh}_3)_3$ ⁵. However, in the presence of triethylaluminum, the reaction of $\text{Pd}(\text{PPh}_3)_4$ with carbon monoxide occurred and gave ill-defined carbonyl complexes. The details are now being investigated.

The infrared spectra of the above three palladium(0) carbonyl complexes (I), (II), and (III) are given in Table 1. The carbonyl stretching frequency (1955 cm^{-1}) of

TABLE I
CHARACTERIZATION DATA OF PALLADIUM(0) CARBONYL COMPLEXES

Compound	Colour	Decomp. ^a (°C)	Pd (%) found (calcd.)	C (%) found (calcd.)	H (%) found (calcd.)	IR ^b $\nu(\text{CO})$ (cm^{-1})
(I) Pd(CO)(PPh ₃) ₃	cream-yellow	110	11.6 (11.55)	71.46 (71.70)	5.13 (4.93)	1955 s
(II) [Pd(CO)PPh ₃] _n	red	73	26.3 (26.82)	57.11 (57.53)	4.17 (3.82)	1850 vs
(III) [Pd ₃ (CO) ₃ (PPh ₃) ₄]	orange-yellow	70	23.2 (21.97)	61.64 (62.00)	4.28 (4.17)	1845 s 1820 vs

^aIn argon atmosphere.

^bKBr disk, s = strong, vs = very strong.

Pd(CO)(PPh₃)₃ is rather lower than the reported value (2018 cm^{-1}) of Pd(CO)(PF₃)(PPh₃)₂¹ which is unstable and not capable of isolation. The large shift of carbonyl stretching frequency suggests a considerable stabilization of the palladium-carbon bond. In fact, the crystals of Pd(CO)(PPh₃)₃ are stable in air for several hours. The infrared spectra of the complexes (II) and (III) show strong bands assignable to bridging carbonyl stretching vibrations. These complexes are less stable than (I).

Molecular weight determinations of the new complexes were unsuccessful due to their low solubilities in benzene, and furthermore, their infrared spectra indicate that they appear to be dissociated in solution. Mass spectra of the three carbonyl complexes gave no useful data since they decomposed on warming, losing carbon monoxide and triphenylphosphine. Therefore the structures of the carbonyl-bridged complexes are still uncertain, but trinuclear structures may be considered in analogy with [Pt₃(CO)₃(PPh₃)₄] and [Pt₃(CO)₃(PPh₂Bz)₃]⁶, and structural studies by X-ray methods are now in progress.

With other tertiary phosphine ligands such as triethylphosphine, tri-n-butylphosphine and ethyldiphenylphosphine, preparations of similar palladium(0) carbonyl complexes were attempted. Although formation of carbonyl complexes could be confirmed from infrared spectra, efforts to obtain pure compounds were unsuccessful.

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