

A Novel Palladium Hydridocarbonyl Anion

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ALTHOUGH chlorocarbonyl species of ruthenium¹ and rhodium² are readily prepared by treating an alcohol solution of the metal halide with carbon monoxide, no such reaction has been reported for palladium. In an attempt to synthesise palladium chlorocarbonyl complexes by such a method we have been able to isolate only what appears to be a palladium hydridocarbonyl anion $[\text{PdH}(\text{CO})\text{Cl}_2]^-$ from the solution. Addition of triphenylarsine to this solution does, however, afford the neutral monocarbonyl complex $[\text{Pd}(\text{CO})(\text{AsPh}_3)\text{Cl}_2]$, while the nitrogen-donor ligands, pyridine and quinoline, do not appear to replace those already present.

When carbon monoxide is bubbled through such a solution in 2-methoxyethanol at room temperature, a yellow colour results. The solution decomposes on standing to give a black material, presumably metallic palladium.

However, immediate addition of tetraphenylarsonium chloride gives a brown diamagnetic carbonyl complex, which is a uni-univalent electrolyte in dimethylformamide. Although the limited solubility of the complex does not permit an investigation of its n.m.r. spectrum in the metal hydride region, the diamagnetic nature of this electrolyte suggests that it may be the palladium(II) hydride, $[\text{AsPh}_4][\text{Pd}(\text{CO})\text{HCl}_2]$. A weak absorption at 1960 cm.^{-1} in the i.r. spectrum is attributable to a metal-hydrogen frequency³ and the strong band at 1900 cm.^{-1} may be assigned to a terminal carbonyl stretching mode.

When ethanol is the solvent used a yellow complex is precipitated on addition of the cation. Although the i.r. spectra of both these compounds are identical in the terminal carbonyl stretching region [$1900\text{s, }1960\text{w cm.}^{-1}$], repeated elemental analyses do not support a similar formulation.

Some properties of the palladium complexes

Compound	Colour	Molar conductivities in 10 ⁻³ M-dimethylformamide solution	ν_{CO} (cm. ⁻¹) (KBr discs)	ν_{M-H} (cm. ⁻¹)
[AsPh ₄][Pd(CO)HCl ₂]	Brown	70	1900s	1960w
[pyH][Pd(CO)HCl ₂],H ₂ O	Yellow-green	69	1920s	2010w
[pyH][Pd(CO)HCl ₂]	Yellow	68	1920s	2010w
[qnH][Pd(CO)HCl ₂]	Yellow-green	71	1925s	2000w
[Pd(PPh ₃)Cl ₂]	Yellow	Insoluble	—	—
[Pd(CO)(AsPh ₃)Cl ₂]	Red	Decomposes	1900(s) ^a 1870(w)	—
[Pd(AsPh ₃) ₂ Cl ₂]	Brown-yellow	Insoluble	—	—

^a In chloroform solution.

When pyridine (py) and quinoline (qn) react with the yellow solution, the air-sensitive hydrido-complexes [pyH][Pd(CO)HCl₂],H₂O and [qnH][Pd(CO)HCl₂], are isolated. Both complexes are uni-univalent electrolytes in dimethylformamide, but their solubility is too low for n.m.r. studies. Bands at 3210, 1640, 1530, 1330, and 1240 cm.⁻¹ in the i.r. spectrum of [pyH][Pd(CO)HCl₂],H₂O indicate a pyridine cation,⁴ and the weak, broad absorption at 3500 cm.⁻¹ is associated with the water molecule. Metal hydride and carbonyl stretching modes may also be assigned (see Table). The spectrum of the quinolinium complex shows absorptions at 2800 and 1640 cm.⁻¹ which can be assigned to N-H vibrations.

Triphenylphosphine replaces both the hydrido- and carbonyl groups to give the known⁵ complex [Pd(PPh₃)₂Cl₂] (irrespective of the alcoholic solvent used). The insolubility of this derivative may give rise to its preferential

formation over hydrido- and carbonyl compounds. Slow addition of a small amount of triphenylarsine (less than 1 mole of ligand per mole of palladium) caused an immediate colour change to red with the precipitation of the red complex [Pd(CO)(AsPh₃)Cl₂], which must be quickly removed since a further reaction occurs, (especially if an excess of ligand is present) to give the brown-yellow insoluble compound [Pd(AsPh₃)₂Cl₂]. The complex [Pd(CO)(AsPh₃)Cl₂] has a similar strong terminal carbonyl band at 1900 cm.⁻¹ as well as a weak broad band at 1875 cm.⁻¹. This latter band may be due to the presence of impurities, although it is possible that the complex is present in more than one geometric form. The absence of the weak band in the region 1960—2050 cm.⁻¹ assigned to metal-hydrogen stretch in the other complexes, is noteworthy.

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