

The Extremely Rapid Acid-catalysed Additions of Acetylenes to $[\text{Pd}_2\text{Cl}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2]$ and the Synthesis of $[\text{Pd}_2\text{Cl}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2(\mu\text{-C}=\text{CH}_2)]$

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The addition of acetylenes such as $\text{HC}\equiv\text{CH}$, $\text{HC}\equiv\text{CPh}$, or $\text{MeOOC}\equiv\text{CCOOMe}$ to $[\text{Pd}_2\text{Cl}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2]$ to give 'dimetallated olefins' is catalysed by traces of acid or methanol but inhibited by a base: the 'dimetallated olefin' complex $[\text{Pd}_2\text{Cl}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2(\mu\text{-HC}=\text{CH})]$ makes an interesting comparison with the vinylidene complex $[\text{Pd}_2\text{Cl}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2(\mu\text{-C}=\text{CH}_2)]$.

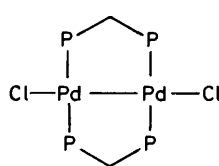
It has been reported that the well-known dipalladium complex, $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2]$ (**1**), $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$, reacts with acetylenes possessing one or two activating (electron-withdrawing) groups, to give 'dimetallated olefin' complexes of the type (**2**):¹ e.g., $\text{CF}_3\text{C}\equiv\text{CCF}_3$, $\text{MeOOC}\equiv\text{CCOOMe}$, or $\text{HC}\equiv\text{CCOOMe}$ give, respectively, (**2a**), (**2b**), or (**2c**). Other acetylenes, without activating groups, such as $\text{PhC}\equiv\text{CH}$, $\text{PhC}\equiv\text{CPh}$, or $\text{HC}\equiv\text{CH}$ failed to react.¹ We have now found that acids, even in trace amounts, catalyse the addition of unactivated acetylenes to the dipalladium bond of (**1**) to a remarkable degree. Thus, while a 0.032 M solution of (**1**) in dry CH_2Cl_2 failed to react with $\text{RC}\equiv\text{CH}$ ($\text{R} = \text{Ph}$ or *p*-tolyl) in a 20-fold excess, over a period of 24 h, the addition of a trace of $\text{HBF}_4\cdot\text{Et}_2\text{O}$, sufficient to make the solution 10^{-3} M in this acid, catalysed the formation of $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2(\mu\text{-HC}=\text{CR})]$ (**2d**) and (**2e**), the conversion being complete in less than 5 min at 20 °C (^{31}P - $\{^1\text{H}\}$ n.m.r. evidence). The adducts (**2d**) and (**2e**) were isolated in 80–95% yield as pale yellow crystalline solids by precipitation with MeOH. Similarly, passage of acetylene through a CH_2Cl_2 solution of (**1**) caused rapid lightening of the solution to pale yellow and $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2(\mu\text{-HC}=\text{CH})]$ (**2f**) was isolated in 70% yield. Adducts of type (**2**) and other complexes described in this communication were fully characterized by elemental analysis and by ^{31}P - $\{^1\text{H}\}$, ^1H , and ^1H - $\{^{31}\text{P}\}$ n.m.r. and i.r. spectroscopy.[†] We also find that acid catalyses the addition of electronegative acetylenes to (**1**). Thus, a 0.019 M solution of (**1**) in CH_2Cl_2 , when treated with a 2-fold excess of $\text{MeOOC}\equiv\text{CCOOMe}$, was converted into the adduct (**2b**) at a rather slow rate, the time for 50% conversion being >1 h, but a similar mixture in the presence of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (10^{-3} M) gave complete conversion into the adduct (**2b**) in <2 min. Moreover, the presence of an excess of base ($\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$) slowed the reaction down to the extent that it was only ca. 50% complete even after 2 weeks at room temperature. MeOH (0.1 M), in place of $\text{HBF}_4\cdot\text{Et}_2\text{O}$, also catalysed the conversion but the reaction was much slower, the half-life being ca. 10 min (^{31}P - $\{^1\text{H}\}$ n.m.r. evidence).

The additions of the acetylenes $\text{HC}\equiv\text{CH}$, $\text{PhC}\equiv\text{CH}$, or *p*-tolyl $\text{C}\equiv\text{CH}$ are reversible; thus on heating benzene solutions of (**2d**), (**2e**), or (**2f**) under reflux for 2 h, (**1**) was produced in high yields. Photolysis of (**2d**) or (**2e**) in CH_2Cl_2 solution, using a fluorescent tube of the 'daylight' type, gave back (**1**), essentially quantitatively, in 12 h: (**2f**) was similarly converted back into (**1**) but more slowly and other, unidentified, products were formed.

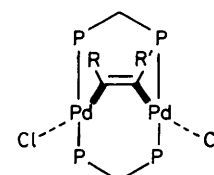
We have also made the vinylidene-bridged complex $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2(\mu\text{-C}=\text{CH}_2)]$ (**3a**), isomeric with (**2f**). This

novel A-frame was made by effecting a double oxidative addition to palladium(0) viz. by heating a mixture of $[\text{Pd}(\text{PPh}_3)_4]$, dppm , and $\text{Cl}_2\text{C}=\text{CH}_2$ in refluxing benzene for 2 h. The complex (**3a**) was obtained, in consistently high (>90%) yields, by this method.[‡] It is thus much more thermally stable than (**2f**) and was also recovered unchanged after irradiation for 12 h with fluorescent light. The chlorides in (**3a**) are readily replaced by bromides or iodides by treatment with NaBr or NaI in acetone, giving (**3b**) or (**3c**), respectively. Treatment of (**3a**) with TIPF_6 and $\text{PhC}\equiv\text{CH}$ gave the diphenylacetylidene complex (**3d**); and treatment with Bu^tNC and ammonium hexafluorophosphate gave $[\text{Pd}_2(\text{CNBu}^t)_2(\mu\text{-C}=\text{CH}_2)(\mu\text{-dppm})_2][\text{PF}_6]_2$.

The vinylidene complex (**3a**),[‡] in CD_2Cl_2 solution, reacts with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (1 mol equiv.), to give a single product, as judged by ^{31}P - $\{^1\text{H}\}$ n.m.r. spectroscopic evidence. The four P-nuclei of this product are inequivalent and the ^1H - $\{^{31}\text{P}\}$ and ^1H n.m.r. spectra are very complex and broad. These data are consistent with this new product having a bridging vinyl group viz. $[\text{ClPd}(\mu\text{-dppm})_2(\mu\text{-}\sigma,\eta^2\text{-CH}=\text{CH}_2)\text{PdCl}]\text{BF}_4$; in which complex the four P-nuclei are non-equivalent and the four dppm methylene hydrogens and the three vinyl hydrogens are

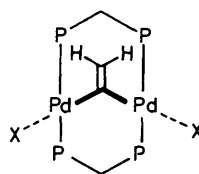


(1)



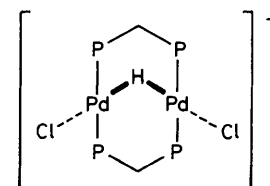
(2)

- a; $\text{R} = \text{R}' = \text{CF}_3$
 b; $\text{R} = \text{R}' = \text{COOMe}$
 c; $\text{R} = \text{H}$, $\text{R}' = \text{COOMe}$
 d; $\text{R} = \text{H}$, $\text{R}' = \text{Ph}$
 e; $\text{R} = \text{H}$, $\text{R}' = \text{C}_6\text{H}_4\text{Me-}p$
 f; $\text{R} = \text{R}' = \text{H}$



(3)

- a; $\text{X} = \text{Cl}$
 b; $\text{X} = \text{Br}$
 c; $\text{X} = \text{I}$
 d; $\text{X} = \text{C}\equiv\text{CPh}$



(4)

[†] E.g. (**2f**): N.m.r. δ_{P} (in CD_2Cl_2) 9.3 p.p.m.; δ_{H} (in CD_2Cl_2) 6.28 ($\text{HC}=\text{CH}$), these were coupled to ^{31}P in a virtual 1:4:6:4:1 quintet, apparent $J(\text{P}-\text{H})$ 15.4 Hz; δ_{H} 3.35 and 2.90 ($\text{PCH}_2\text{H}_2\text{P}$), $^2J(\text{H}_A-\text{H}_X)$ 12.7 Hz, each of these protons was coupled to four ^{31}P nuclei giving virtual 1:4:6:4:1 quintets, apparent $J(\text{P}-\text{H})$ 5.4 and 3.4 Hz respectively; i.r. $\nu(\text{Pd}-\text{Cl})$ 273 cm^{-1} .

[‡] (**3a**): N.m.r. δ_{P} (CD_2Cl_2) 15.6 p.p.m.; δ_{H} (CDCl_3) 5.14 ($=\text{CH}_2$) these protons were coupled to the four P-nuclei giving a virtual 1:4:6:4:1 quintet with apparent $J(\text{P}-\text{H})$ 11.0 Hz; δ_{H} 3.42 and 2.56 ($\text{PCH}_2\text{H}_2\text{P}$), $^2J(\text{H}-\text{H})$ 12.8 Hz, each of which was virtually coupled to all four P-nuclei with apparent coupling constants of 5.6 and 3.1 Hz, respectively; i.r. $\nu(\text{Pd}-\text{Cl})$ 262 cm^{-1} .

also non-equivalent. The data exclude a carbyne bridged complex *viz.* $[\text{ClPd}(\mu\text{-dppm})_2(\mu\text{-C-CH}_3)\text{PdCl}]\text{BF}_4$. The product is labile and we were unable to isolate it pure. When its solution was treated with base (Et_3N) it immediately gave a complex mixture containing some of the starting complex (**3a**).

We suggest that on addition of acid, or a source of protons, some of the dipalladium complex (**1**) is converted into the protonated species $[\text{ClPd}(\mu\text{-dppm})_2(\mu\text{-H})\text{PdCl}]^+$ (**4**) and this is what reacts so rapidly with acetylenes. However at this stage we cannot suggest why the protonated complex is so much more reactive than the non-protonated complex. The corresponding platinum complex $[\text{ClPt}(\mu\text{-dppm})_2(\mu\text{-H})\text{PtCl}]^+$ is well-known² and has recently been shown often to be present in $[\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2]$, with which it undergoes an extremely rapid proton transfer reaction.³ When we treated (**1**), $\delta_{\text{P}} -3.7$ p.p.m., with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (1 mol equiv.) in CD_2Cl_2 , a single but labile product, with equivalent P-nuclei, $\delta_{\text{P}} +11.8$ p.p.m.,

was formed. It seems likely that this is $[\text{ClPd}(\mu\text{-dppm})_2(\mu\text{-H})\text{PdCl}]^+$ but we have failed to isolate it pure as either the BF_4 or BPh_4 salts and could not detect a high field (hydride) resonance in the ^1H or $^1\text{H}\{-^3\text{P}\}$ n.m.r. spectra (at 300 or 213 K): we suggest that the reason for this is extremely rapid exchange between the hydride and protons in solution, even at low temperatures.

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