A Palladium Hydride and Germyl–Palladium Complexes

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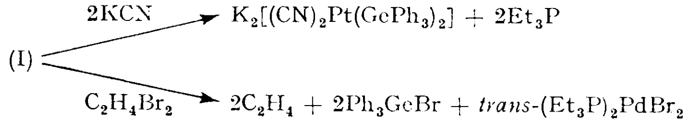
THE high thermal stability of platinum–carbon[1] and platinum–hydrogen complexes[2] is paralleled by complexes containing platinum–germanium bonds (*e.g. cis-* and *trans-*$(Et_3P)_2Pt(GePh_3)_2$ and $(Et_3P)_2Pt(H)GePh_3$.[3–5] Palladium–carbon complexes are characteristically of much lower thermal stability, especially in solution.[6] We now find that organogermyl palladium complexes formed by the reaction:

$$L_2PdX_2 + 2Ph_3GeLi \rightarrow L_2Pd(GePh_3)_2 \qquad \text{(I)}$$

[L = Et_3P, Ph_3P, bipy, 1,2-bis(diphenylphosphino)-ethane] are also of low thermal stability and only the bistriethylphosphine complex (I) has been obtained in a pure form. This complex, which is stable to hydrolysis and atmospheric oxidation at −40°, decomposes thermally even at −20° in solution. The solid decomposed above 97° to give products typical of radical intermediates:

$$\text{(I)} \xrightarrow{97^\circ} C_6H_6 + Ph_6Ge_2 + Ph_4Ge + Et_3P + C_2H_4 + H_2 + Pd.$$

It did not react with hydrogen under mild conditions, but with potassium cyanide it formed a much more stable anionic complex without cleavage of the metal–metal bonds. Cleavage by 1,2-dibromoethane was quantitative.



$$\begin{tikzcd} & K_2[(CN)_2Pt(GePh_3)_2] + 2Et_3P \\ \text{(I)} \arrow[ur, "2KCN"] \arrow[dr, "C_2H_4Br_2"'] & \\ & 2C_2H_4 + 2Ph_3GeBr + trans\text{-}(Et_3P)_2PdBr_2 \end{tikzcd}$$

Hydrogen chloride, in contrast to the platinum analogue,[4,5] gave only two products, Ph_3GeH and *trans-*$(Et_3P)_2PdCl_2$. However separation of triphenylgermane by sublimation indicated a further reaction involving the formation of a Pd–H compound. Closer study using trimethylgermane and *trans-*$(Et_3P)_2PdCl_2$ at 40° led to the isolation of the pure hydropalladium chloride complex, $(Et_3P)_2Pd(H)Cl$ (previously obtained in a crude state[7]) as colourless octahedral prisms, dec. 55° (νPd–H, 2035; δ PdH, 721 cm.$^{-1}$). This complex, which decomposed over 5 minutes at 20° in benzene solution, sublimed (45°/10^{-6}mm.) without appreciable decomposition. The overall reaction was complex and indicative of radical processes:

$$Me_3GeH + (Et_3P)_2PdCl_2 \rightarrow (Et_3P)_2Pd(H)Cl + Me_6Ge_2 + Me_3GeCl + H_2 + Pd$$

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