'Bis(triphenylphosphine)palladium:' Its Generation, Characterization, and Reactions

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Pd^0–PPh_3 complexes obtained by reduction of $X_2Pd(PPh_3)_2$, where X is Cl, Br, or I, with various reducing agents, *e.g.*, RLi and $Bu^i{}_2AlH$, are neither free $Pd(PPh_3)_2$ nor its polymer, those derived from RLi being consistent only with $LiXPd(PPh_3)_2$, $Li_2X_2Pd(PPh_3)_2$, and aggregates thereof.

Palladium–PPh_3 complexes, such as $Pd(PPh_3)_4$ and $Cl_2Pd(PPh_3)_2$, have been shown to be effective precatalysts for cross coupling.[1] A 14-electron species, '$Pd(PPh_3)_2$,' has been implicated as the actual catalyst undergoing oxidative addition with organic halides.[1] Although some di-co-ordinate Pd complexes of the $Pd(PR_3)_2$ type containing bulky ligands, such as $PBu^t{}_3$, have been fully characterized,[2] no characterization of '$Pd(PPh_3)_2$' by spectroscopic means has been reported.

Treatment of $Cl_2Pd(PPh_3)_2$ with 2 equiv. of an organolithium reagent, *e.g.*, MeLi, PhLi, or $Bu^tCH{=}CHLi$, in tetrahydrofuran (THF) under nitrogen gives a common product (**1**) showing only one ^{31}P n.m.r. signal at 23.0—23.3(s) p.p.m. (relative to 85% H_3PO_4) along with a homocoupled product, *e.g.*, MeMe, PhPh, or $(Bu^tCH{=}CH)_2$, respectively, in $\geqslant$95% yields. The same species (**1**) can also be generated by the reaction of $Cl_2Pd(PPh_3)_2$ with 2 equiv. of Bu^nLi. The organic product in this case, however, is a mixture of n-octane, n-butane, and but-1-ene. Clearly, (**1**) is independent of the organic group in the organolithium reagent. A solution containing (**1**) has yielded the following additional spectral data: i.r. (THF) 3075 (m), 3058 (m), 1596 (m), 1479 (m), 1434 (s), 744 (s), and 696 (s) cm^{-1}; ^1H n.m.r. (THF),δ 6.9—7.5 (m, 30 H).

The reactions of (**1**) with PPh_3 (1 or 2 equiv.), PhI, and maleic anhydride cleanly and quantitatively produce $Pd(PPh_3)_3$[3] (^{31}P n.m.r. 20.5 p.p.m.) or $Pd(PPh_3)_4$[4] (15.8 p.p.m.), $PhPd(PPh_3)_2I$[5] (23.8 p.p.m.), and $(Ph_3P)_2$-$Pd(C_4H_2O_3)$[6] (27.5 p.p.m.), respectively. These results indicate that (**1**) consists entirely or partially of the $Pd(PPh_3)_2$ unit. The ^{31}P n.m.r. spectrum of (**1**) does not detectably change for at least several hours at ambient temperature, indicating that (**1**) is stable under these conditions. However, all attempts to isolate (**1**) led to its decomposition, as judged by ^{31}P n.m.r. spectroscopy. Consequently, no elemental analytical and molecular weight information is available at present.

Since THF, N_2, and LiCl, formed as a byproduct, are the only compounds in the reaction mixture other than (**1**) and the innocuous hydrocarbon byproducts, possible roles of these compounds in (**1**) were examined. To this end, the reaction of $Cl_2Pd(PPh_3)_2$ with 2 equiv. of Bu^nLi was carried out both in toluene under N_2 and in THF under argon. The Pd-containing product in either case shows the same ^{31}P n.m.r. singlet in the 23.0—23.3 p.p.m. range. Thus, neither THF nor N_2 appreciably interacts with '$Pd(PPh_3)_2$.' However, LiX (X = Cl, Br, or I) must interact significantly with '$Pd(PPh_3)_2$,' since the use of $Br_2Pd(PPh_3)_2$[7] and $I_2Pd(PPh_3)_2$[7] in place of $Cl_2Pd(PPh_3)_2$ shifts the ^{31}P n.m.r. signal to 22.0 and 15.8 p.p.m., respectively. In each case, addition of 1 equiv. of PhI induces clean formation of $PhPd(PPh_3)_2I$ (23.8 p.p.m.). We conclude that the Pd-containing product in the reaction of $X_2Pd(PPh_3)_2$ with 2 equiv. of RLi is neither free $Pd(PPh_3)_2$ nor its polymer. The only structures that are consistent with the available data are $LiXPd(PPh_3)_2$, $Li_2X_2Pd(PPh_3)_2$, and aggregates thereof. Clearly, the exact structure of '$Pd(PPh_3)_2$' depends on the reagents used to generate it. For example, treatment of $Cl_2Pd(PPh_3)_2$ with 2 equiv. of $Bu^i{}_2AlH$ in THF cleanly produces a Pd–PPh_3 complex showing only the ^{31}P n.m.r. signal at 21.8 p.p.m., which acts as '$Pd(PPh_3)_2$.' Typically, its treatment with 1 equiv. of PhI quantitatively produces $PhPd(PPh_3)_2I$ (23.8 p.p.m.). Finally, several samples of '$Pd(PPh_3)_2$' generated from different precursors have been shown to exhibit catalytic activities in cross coupling indistinguishable from one another.

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