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Preliminary communication

Metal atom reactions with fluorocarbons
III*. Insertion of palladium atoms into aryl carbon–halogen bonds

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Recent work by Skell and his coworkers[2], Timms[7], and work in our laboratories[3] has shown that metal atom reactions with organic compounds provide a new method for direct synthesis of organometallic compounds. Our initial publication in this area illustrated that zinc atoms were capable of oxidative insertion into R_f–I bonds. In this communication we show that palladium, a transition metal, is also capable of oxidative C–X bond addition. A novel non-ligand stabilized structure of the elements $(C_6F_5PdBr)_n$ has been prepared, isolated, and used in further synthesis.

Codeposition of palladium atoms with a high excess of bromopentafluorobenzene at –196° followed by warming to room temperature with pump off of excess C_6F_5Br yielded a heavy orange-brown oil which slowly solidified. This material was stable to air and water for short periods of time, and could be taken up in solvents (moderately soluble in benzene, ethyl ether and methylene chloride, and very soluble in acetone) to form orange solutions. Its infrared spectrum in benzene showed low frequency absorptions at 406 and 546 cm^{-1} (possible Pd–C)[4] and other intense bands at 1520s, 1505vs, 1670s, 1268s, 1300s, 1082vs, 1070s, 965s, and 800 cm^{-1}. Decomposition mass spectroscopy (probe 180°) showed the ions $PdBr_2^+$, $C_{12}F_{10}^+$, $C_{12}F_9^+$, and $C_6F_5^+$. Chlorination of this material yielded chloropentafluorobenzene. Dissolved in benzene, the brown-orange material decomposed over a four hour period yielding decafluorobiphenyl ($C_{12}F_{10}$), palladium dibromide ($PdBr_2$), and palladium metal in ratios 1/1/1. Addition of triphenylphosphine (in benzene) to a fresh solution of this material yielded immediately a white solid bis(triphenylphosphine)pentafluorophenylpalladium bromide (I), 13%**, m.p. 265–267°. Found: C, 57.62; H, 3.45; Br, 9.15. Calcd.: C, 57.49; H, 3.44; Br, 9.10%. IR (cm^{-1}) 1500vs, 1460vs, 1100s, 1050s, 950s, 935s, 690vs; NMR τ 3.0 (multiplet, 18 H), τ 2.2 (multiplet, 12 H). We assume I is *trans* since a similar reaction with dimethylphenylphosphine yielded *trans*-bis(dimethylphenyl-

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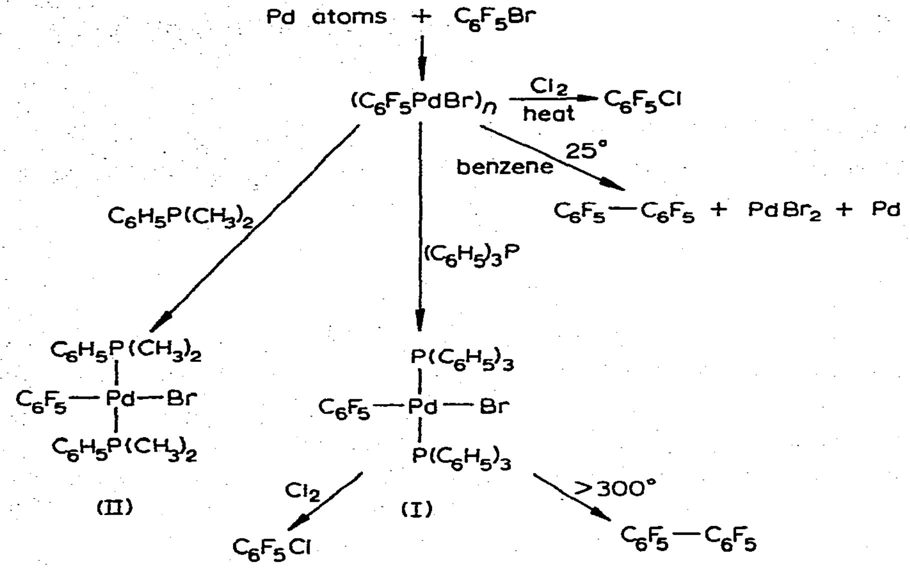
*For part II see ref. 1.

**Yields are based on metal vaporized and corrected since only 60% of the metal vapor reaches the reaction zone.

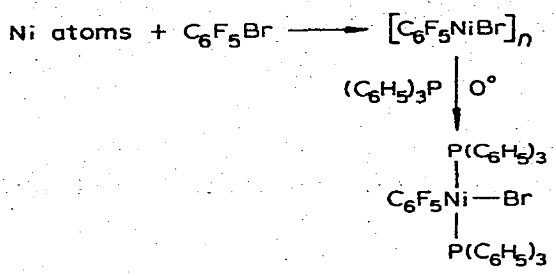
phosphine)pentafluorophenylpalladium bromide (II), 33%, m.p. 140–141°. IR (cm^{-1}) 1520vs, 1480vs, 1455vs, 1440s, 1375s, 1300s, 1128s, 1075vs, 985vs, 928vs, 860s, 805vs, 755vs, 735s, 710vs, 485s, and 425s; NMR τ 8.68 (triplet, 12 H), J(P–H) 3.5 Hz; τ 3.05 (multiplet, 10 H). The *trans* configuration is evident from the P–H coupling yielding a triplet[5].



Although the [C_6F_5PdBr] structure probably exists in a dimeric or polymeric bridged form in the solid state, in solution there are very reactive open sites available, as shown by the instantaneous phosphine reactions. Other coordination chemistry of this interesting intermediate is being investigated.

Palladium atoms also react with bromobenzene, but the resultant compound is unstable, and liberates biphenyl on being warmed to room temperature. Obviously, the pentafluorophenyl group greatly stabilizes the Ar–Pd–Br moiety.

We find great similarities between palladium atoms and nickel atoms in these reactions. Thus, nickel atoms with bromobenzene or bromopentafluorobenzene yielded biphenyl or decafluorobiphenyl respectively on being warmed. In these cases, the coupling reaction occurred below room temperature. However, at 0° a trapping experiment was at least partially successful. That is, nickel atoms and C_6F_5Br were allowed to react and the excess C_6F_5Br was pumped off on slow warming to 0°. Then a benzene solution of triphenylphosphine was added, and white bis(triphenylphosphine)pentafluorophenylnickel bromide (III) was found, 2.6%, m.p. 196–198°C in agreement with the literature[6].



(III)

Thus, we have shown that the metal atom technique allows the production of ArMX compounds (M = Ni, Pd) under inert conditions and relatively low temperatures. Reaction of the bulk metal with ArBr does not produce these compounds under conditions that allow isolation of the material. Both Heck[8] and Henry[9] have carried out interesting work where similar structures were considered as intermediates, but these were not isolated.

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