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An Aryldiazenido Complex of Palladium: Insertion of Aryldiazonium Cation into a Pd^I–Pd^I Bond

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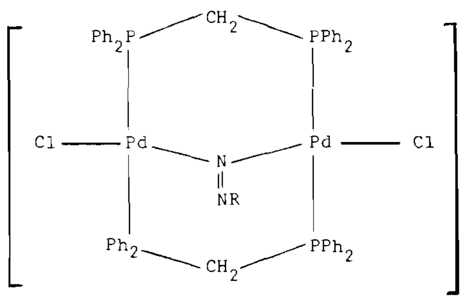
Despite the considerable current interest in aryldiazenido-complexes of transition metals, and the variety of metals for which such complexes have been synthesized, no example of a corresponding palladium complex has hitherto been reported [1]. Palladium(II) complexes such as [Pd(PEt$_3$)$_2$Cl$_2$], [{Pd(PEt$_3$)$_2$Cl}$_2$][BF$_4$]$_2$, [PdCl(η^3-C$_3$H$_5$)]$_2$, or PdCl$_2$ do not react with aryldiazonium ions, and K$_2$[PdCl$_4$] merely undergoes metathesis to produce the aryldiazonium tetrachloropalladate. Oxidative addition of diazonium ions to zero-valent palladium complexes such as [Pd(PPh$_3$)$_4$] may initially produce aryldiazenido complexes, but extrusion of nitrogen occurs spontaneously, and aryl palladium complexes result [2]. Other examples which we have found to behave similarly are [Pd(dba)$_2$], [Pd(dba){P(C$_6$H$_{11}$)$_3$}$_2$], and [Pd(dba)(PBu$^n_3$)$_2$] (dba = dibenzylideneacetone).

Recently, palladium(I) complexes [Pd$_2$(dppm)$_2$X$_2$] and [Pd$_2$(dam)$_2$X$_2$] (dppm = Ph$_2$PCH$_2$PPh$_2$; dam = Ph$_2$AsCH$_2$AsPh$_2$; X = Cl, Br) have been synthesized and the dppm complex shown by X-ray crystallography to be binuclear with a Pd–Pd bond [3, 4]. We have found that the dppm complex (X = Cl) reacts smoothly with diazonium tetrafluoroborates or hexafluorophosphates at room temperature without extrusion of nitrogen to yield 1:1 complexes of the general type [Pd$_2$(dppm)$_2$(N$_2$R)Cl$_2$]Y (where R = o-CF$_3$C$_6$H$_4$; p-CF$_3$C$_6$H$_4$; o-NO$_2$C$_6$H$_4$; p-FC$_6$H$_4$; o-CH$_3$OC$_6$H$_4$; Y = BF$_4$, PF$_6$).

Results and Discussion

The orange crystalline complexes are 1:1 electrolytes of appropriate molecular weight in CH$_2$Cl$_2$, and are air-stable as solids, or in solution for at least 48 h. The least stable one has the electron-releasing OCH$_3$ substituent. We assign the structure I to these complexes, possessing two palladium atoms bridged by the N$_2$R ligand on the following evidence. The reaction is analogous to the addition of CO or RNC to give [Pd$_2$(dppm)$_2$(CO)X$_2$] and [Pd$_2$(dppm)$_2$(CNR)X$_2$] in which the CO and RNC ligands occupy bridging positions [5]. This reaction could be reversed for CO but not for RNC, and we find the diazonium addition to be irreversible. The complexes may also be obtained by displacing the CO ligand from the bridging position by diazonium ions, and this process can neither be reversed with CO, nor is CO incorporated, suggesting that the aryldiazenide ligand is now occupying the bridging position. Whereas the proton decoupled ^{31}P nmr spectrum of [Pd$_2$(dppm)$_2$Cl$_2$] shows all phosphorus atoms to be equivalent, the diazenide complex gives an AA'BB' spectrum consistent with a bridging diazenide ligand with an NNC angle less than 180°. In the two currently known examples [6, 7] of a bridging N$_2$R ligand this angle is 110–120°. A bridging N$_2$R ligand was previously obtained [7] by the insertion of a diazonium ion into the Ir–Ir bond in the complex [Ir$_2$O(NO)$_2$(PPh$_3$)$_2$], and the present reaction appears to be analogous, and only the second example of this type of process.



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The infrared spectrum does not exhibit any band assignable to ν(NN) as was also the case for the iridium complex. Treatment with HCl or chloride displaces the diazenide ligand giving [Pd(dppm)Cl$_2$], which also has been isolated from decomposed solutions of the complex in CH$_2$Cl$_2$.

Experimental

Preparation of [Pd$_2$(dppm)$_2$(N$_2$R)Cl$_2$][BF$_4$]

A suspension of [Pd$_2$(dppm)$_2$Cl$_2$] (0.20 g; 1.85 × 10^{-4} mol) in acetone (20 ml) was stirred at room temperature with one equivalent of the diazonium salt under N$_2$ for 30 min. The solution was filtered and solvent removed under vacuum until crystallization occurred. Filtration gave the complex as an orange solid which was washed with ethanol and recrystallized from dichloromethane–ether. Typical analyses were (a) R = o-CF$_3$C$_6$H$_4$, p-CF$_3$C$_6$H$_4$: Calcd. for [Pd$_2$(Ph$_2$PCH$_2$PPh$_2$)$_2$(N$_2$C$_6$H$_4$CF$_3$)Cl$_2$][BF$_4$] C, 52.16; H, 3.69; N, 2.14%. Found: C, 52.24; H, 3.92; N, 2.00 (o-CF$_3$) and C, 52.26; H, 3.88; N, 2.1% (p-CF$_3$). (b) R = p-F, Calcd. for [Pd$_2$(Ph$_2$PCH$_2$PPh$_2$)$_2$(N$_2$C$_6$H$_4$F)Cl$_2$][BF$_4$] C, 50.93; H, 3.66; N, 2.12%. Found: C, 50.95; H, 3.85; N, 2,22%. Electrical conductivities were measured on *ca.* 1 × 10^{-3} *M* solutions in nitromethane and ranged 70–85 ohm^{-1} cm^2. Apparent molecular weights were measured on *ca.*

5×10^{-3} M solutions in CH_2Cl_2 by osmometry and showed the expected lowering from theoretical values (in parentheses): M 1086 (1312; o-CF_3), 1025 (1312; p-CF_3), 888 (1289; o-NO_2), 813 (1274; o-OCH_3). The apparent M approached the theoretical values with increasing concentrations.

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