Journal of Organometallic Chemistry, 246 (1983) C83—C84
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

CHEMICAL BEHAVIOUR OF TETRAHYDROFURAN IN THE PRESENCE OF THE $Pd(C_6F_5)_2$ MOIETY

G. LOPEZ, G. GARCIA, J. RUIZ and N. CUTILLAS
Department of Inorganic Chemistry, University of Murcia, Murcia (Spain)

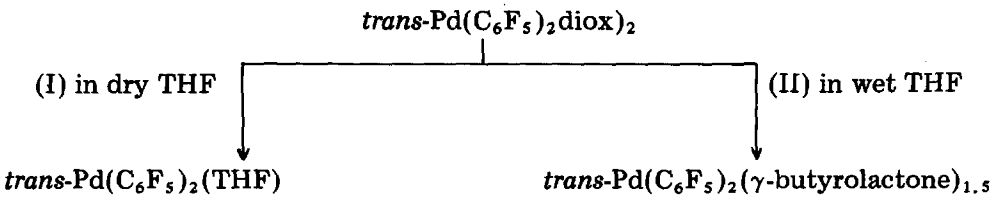
(Received January 4th, 1983)

Summary

Treatment of *trans*-$Pd(C_6F_5)_2$(dioxane)$_2$ with dry THF leads to the isolation of *trans*-$Pd(C_6F_5)_2$(THF). However, the same reaction carried out in wet THF results in the oxidation of THF to γ-butyrolactone, the isolated complex being *trans*-$Pd(C_6F_5)_2$(γ-butyrolactone)$_{1.5}$.

Recently, we reported the preparation of the dioxanates *trans*-$M(C_6F_5)_2$(diox)$_2$ (M = Pd [1], Pt [2]; diox = 1,4-dioxane) and their use for the preparation of labile complexes of the type *trans*-$M(C_6F_5)_2$(solvent)$_x$ in which solvent is a weak O-donor ligand such as dimethylformamide and dimethylsulfoxide [2]. We now report on the behaviour of tetrahydrofuran in the presence of the $Pd(C_6F_5)_2$ moiety.

When *trans*-$Pd(C_6F_5)_2$(diox)$_2$ is dissolved in tetrahydrofuran the identity of the solid isolated from solution depends on experimental conditions used:

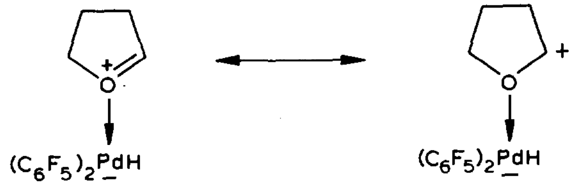


In I a solution of *trans*-$Pd(C_6F_5)_2$(diox)$_2$ (100 mg; 1.16 mmol) in rigorously dried THF (5 ml) was stirred overnight at ca. 15°C. Precipitation with hexane afforded a white solid, which was dried in the air and identified as *trans*-$Pd(C_6F_5)_2$-(THF). Found: C, 38.1; H, 1.7. $Pd(C_6F_5)_2(C_4H_8O)$ calcd.: C, 37.5; H, 1.6%.) Its IR spectrum showed absorptions assignable to THF at 2980—2860s, and 910s cm^{-1} The ^{1}H NMR spectrum of an acetone-d_6 solution (two single resonances at δ

3.61 and 1.79 ppm from TMS) was almost identical with that of free THF, and thus different from that of the complex $(C_6F_5)_2Ni(THF)_2$ [3].

In wet tetrahydrofuran (experiment II) the result was quite different. On refluxing for 3 h a THF/H_2O (5 ml/0.1 ml) solution containing 100 mg of *trans*-$Pd(C_6F_5)_2(diox)_2$ metallic palladium was formed. This was filtered off, the solution was reduced to a small volume under vacuum, and hexane was added, to give a white solid which was identified as *trans*-$Pd(C_6F_5)_2(\gamma\text{-butyrolactone})_{1.5}$. (Found: C, 37.8; H, 1.6. $Pd(C_6F_5)_2(C_4H_6O_2)_{1.5}$ calcd.: C, 37.9; H, 1.6%.) The IR spectrum of the compound showed the relevant absorptions of the neutral ligand at 1755vs cm^{-1} (C=O stretching; 1770 in liquid γ-butyrolactone) and a double band at 1200—1190 cm^{-1} (s; C(=O)—O stretching). The neutral ligand was also identified by GLC and ^1H NMR. In acetone-d_6 the lactone compound gave a complex multiplet at δ 2.40 and a triplet at δ 4.35 ppm (J 6.5 cps) from TMS.

The IR spectra of both compounds showed the following bands assignable to C_6F_5 group [4]: 1630m, 1605m, 1490vs, 1355m, 1320s, 1305s, 1280m, 1045vs, 1030vs, 950vs, and 760vs cm^{-1}. The linearity of the C—Pd—C skeleton is suggested by the presence of a single band in the range 800—750 cm^{-1} [1,2]. As mentioned elsewhere [2], both the pattern of IR bands and the stoichiometries of the compounds strongly suggest the presence of structures involving C_6F_5 bridges.



A number of reagents (e.g., Br_2, Ph_3C^+ [5], RuO_4 [6]) are known to oxidize ethers. We think, however, that the transformation reported herein closely parallels the β-hydrogen abstraction from ethers observed in transfer-hydrogenation reactions [7,8]. Thus the conversion could proceed through the formation of a monohydrido complex and further attack of the H_2O nucleophile on the resulting carbonium ions. In fact, when the same reaction was carried out with *trans*-$Pt(C_6F_5)_2(diox)_2$ a solid mixture was isolated which showed an IR absorption assignable to a Pt—H bond (at ca. 2100 cm^{-1}), but its low solubility in common solvents prevented us from obtaining ^1H NMR data.

References

1 G. Garcia and G. López, Inorg. Chim. Acta, 52 (1981) 87.
2 G. López, G. Garcia, N. Cutillas and J. Ruiz, J. Organometal. Chem., 241 (1983) 269.
3 R.G. Gastinger, B.B. Anderson, and K.J. Klabunde, J. Am. Chem. Soc., 102 (1980) 4959.
4 D.A. Long and D. Steele, Spectrochim. Acta, 19 (1963) 1955.
5 N.C. Deno and N.H. Potter, J. Am. Chem. Soc., 89 (1967) 3550.
6 L.M. Berkowitz and P.N. Rylander, J. Am. Chem. Soc., 80 (1958) 6682.
7 T. Nishiguchi and K. Fukuzumi, J. Am. Chem. Soc., 96 (1974) 1893.
8 C. Masters, A.A. Kiffen and J.P. Visser, J. Am. Chem. Soc., 98 (1976) 1357.