

Preliminary communication

CHEMICAL BEHAVIOUR OF TETRAHYDROFURAN IN THE PRESENCE OF THE $\text{Pd}(\text{C}_6\text{F}_5)_2$ MOIETY

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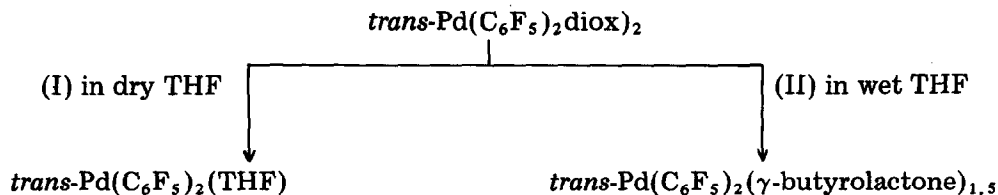
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Summary

Treatment of $\text{trans-Pd}(\text{C}_6\text{F}_5)_2(\text{dioxane})_2$ with dry THF leads to the isolation of $\text{trans-Pd}(\text{C}_6\text{F}_5)_2(\text{THF})$. However, the same reaction carried out in wet THF results in the oxidation of THF to γ -butyrolactone, the isolated complex being $\text{trans-Pd}(\text{C}_6\text{F}_5)_2(\gamma\text{-butyrolactone})_{1.5}$.

Recently, we reported the preparation of the dioxanates $\text{trans-M}(\text{C}_6\text{F}_5)_2(\text{diox})_2$ ($\text{M} = \text{Pd}$ [1], Pt [2]; $\text{diox} = 1,4\text{-dioxane}$) and their use for the preparation of labile complexes of the type $\text{trans-M}(\text{C}_6\text{F}_5)_2(\text{solvent})_x$ 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 $\text{Pd}(\text{C}_6\text{F}_5)_2$ moiety.

When $\text{trans-Pd}(\text{C}_6\text{F}_5)_2(\text{diox})_2$ is dissolved in tetrahydrofuran the identity of the solid isolated from solution depends on experimental conditions used:

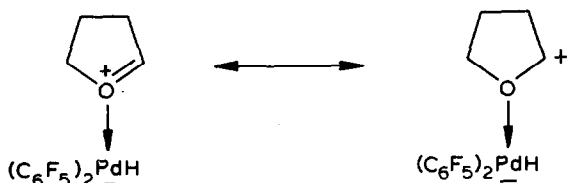


In I a solution of $\text{trans-Pd}(\text{C}_6\text{F}_5)_2(\text{diox})_2$ (100 mg; 1.16 mmol) in rigorously dried THF (5 ml) was stirred overnight at ca. 15°C. Precipitation with hexane afforded a white solid, which was dried in the air and identified as $\text{trans-Pd}(\text{C}_6\text{F}_5)_2(\text{THF})$. Found: C, 38.1; H, 1.7. $\text{Pd}(\text{C}_6\text{F}_5)_2(\text{C}_4\text{H}_8\text{O})$ calcd.: C, 37.5; H, 1.6%. Its IR spectrum showed absorptions assignable to THF at 2980–2860s, and 910s cm^{-1} . The ^1H 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 re-fluxing for 3 h a THF/H₂O (5 ml/0.1 ml) solution containing 100 mg of *trans*-Pd(C₆F₅)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(C₆F₅)₂(γ-butyrolactone)_{1.5}. (Found: C, 37.8; H, 1.6. Pd(C₆F₅)₂(C₄H₆O₂)_{1.5} calcd.: C, 37.9; H, 1.6%.) The IR spectrum of the compound showed the relevant absorptions of the neutral ligand at 1755 vs 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 C₆F₅ 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 C₆F₅ bridges.



A number of reagents (e.g., Br₂, Ph₃C⁺ [5], RuO₄ [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 H₂O nucleophile on the resulting carbonium ions. In fact, when the same reaction was carried out with *trans*-Pt(C₆F₅)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

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