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ON THE VARIOUS FORMS OF PALLADIUM DIACETATE

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Summary. Two forms of palladium diacetate have been prepared and characterized by X-ray crystallography.

Recently we reported[1] that many aryl derivatives of Bi^{III} and of Bi^{V} are quantitatively coupled by Pd° to give diaryls and Bi°. These reactions can be made catalytic. Similarly, arylantimony^{V} and arylleadd^{IV} compounds could be coupled in the same way, giving metallic antimony and lead. However, for these compounds, a stoichiometric amount of Pd° was needed.

In an extension of this work, we recently described[2] the ligand coupling of various tellurides (with extrusion of tellurium) by stoichiometric Pd°. Not only were aryl groups coupled, but even alkyl groups could be coupled to aryl groups or to other alkyl groups in good yield. There is evidence in the literature that ligand variation on Pd^{II} can influence the ratio of coupling to β-elimination[3]. However, the latter is a more common process.[4]

When we wished to extend the scope of this coupling, we were surprised to find a number of commercial samples of palladium diacetate which gave β-hydrogen elimination and not coupling. However, all specimens converted dianisyl telluride in high yield to dianisyl and Te°.

Perplexed by these observations we decided to prepare our own palladium acetate. The literature procedure involves heating a mixture of acetic acid, nitric acid and palladium black under reflux for 17 hrs. until all the nitric acid is consumed. Any unreacted palladium is removed by filtration and the acetic acid is evaporated in vacuo. Recrystallisation from methylene dichloride-hexane is reported to give palladium diacetate m.p. 205°.

When we repeated this preparation, we obtained fine red crystals of palladium diacetate decomposing at 235° to give a palladium mirror. An X-ray analysis of this material showed it to be the known[6] $[Pd(OAc)_2]_6.H_2O$ with an identical X-ray pattern. The authors of this analysis[6] thank the authors[5] of the preceding reference for the sample of palladium diacetate, said to melt at 205°. The simplest explanation of this discrepancy is that the best crystal was selected for the analysis, and this happened to be that of the less soluble 235° palladium diacetate.

Concentration of the mother liquors afforded a different kind of palladium diacetate as fine yellow needles, which decomposed at 205° to a black powder without mirror formation. This is probably the form of palladium diacetate originally reported.[5] An X-ray analysis of this material showed it to be $[Pd(OAc)_2]_3.CH_2Cl_2$, a complex not hitherto reported. Other palladium diacetate complexes described in the literature[7] are $[Pd(OAc)_2]_6.C_6H_6$ and $[Pd(OAc)_2]_6.CH_2Cl_2$. The decomposition behavior of these complexes is not mentioned, but we would expect the benzene complex to give a palladium mirror. The black powder formed by decomposition of 205° palladium diacetate contains palladium dichloride and it is for this reason that it does not melt.

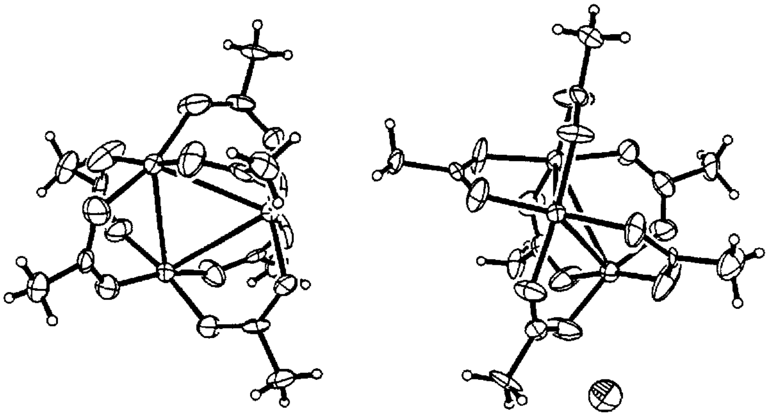

Fig. 1 Ortep diagram of $[Pd(OAc)_2]_6.H_2O$

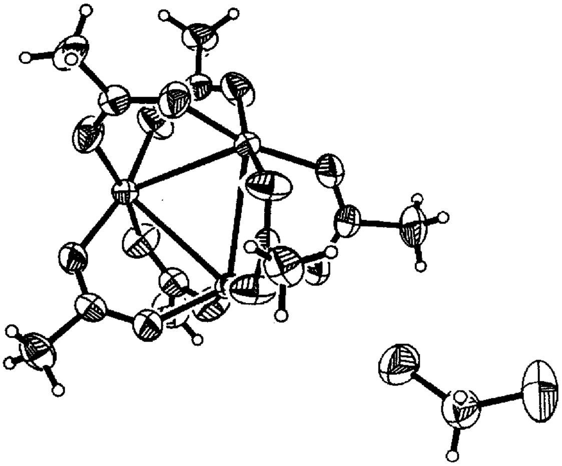

Fig. 2. Ortep diagram of $[Pd(OAc)_2]_3.CH_2Cl_2$

The crystal form of our 205° palladium diacetate is trinuclear, orthorhombic with D_{3h} symmetry. Ortep drawings of the two complexes are given in Figures 1 and 2. Both the 235° and 205° palladium diacetate smoothly coupled aryl groups and extruded Te°. The former never coupled alkyl groups. On four occasions we obtained 205° palladium diacetate which smoothly coupled alkyl groups (experiments by J.K., M.R., and J.C.S.) with extrusion of Te°. However, on many other occasions we did not succeed. It is clear that Pd° is reacting with the CH_2Cl_2 to give an undefined species with the previously observed ability to extrude Te° and couple alkyl groups. Since, in any case, the reaction is stoichiometric in Pd° and it cannot be made catalytic, it is not of much value in synthesis.

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