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Reaction of Bis(Dialkylglyoximato)palladium(II) Complexes with Phosphines

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The readiness of many low-spin, planar nickel(II) complexes to behave as Lewis acids, forming high-spin, 5- or 6-coordinate base adducts, is not shown by corresponding palladium or platinum complexes because of the much greater energy barrier to spin change. When we found recently [1] that low-spin, planar complexes of nickel(II) with dialkylglyoximes and their $-BF_2$-bridged derivatives react with bases to form 5-coordinate adducts in which the low-spin configuration is retained, we were prompted to carry out a study of the corresponding palladium compounds.

The palladium glyoximato complexes are similar to those with nickel and also have low-spin, 4-coordinate O–H···O bridged structures [2, 3], but it has been found much more difficult to replace these bridges by $O{-}BF_2{-}O$ bridges than in the nickel complexes [4] and we were not able to isolate $-BF_2$-bridged palladium complexes of sufficient purity for satisfactory quantitative studies.

Solutions of bis(glyoximato)palladium complexes in benzene or acetonitrile solutions are pale yellow and become red on addition of bases, such as pyridine, 2,2′-bipyridine or 1,10-phenanthroline, suggesting that adducts are formed, but calorimetric studies of these reactions revealed no measurable evolution of heat, so that the adducts formed are probably of very low stability. Similar colour changes on addition of phosphines, particularly trialkylphosphines, were however accompanied by evolution of heat and these reactions were studied calorimetrically.

Calorimetric titration of bis(ethylmethylglyoximato)palladium(II) with tributylphosphine gave enthalpograms which could not be interpreted simply in terms of the formation of a 1:1 adduct, but required the assumption that both 1:1 and 1:2 adducts were formed together. In benzene solution at 30 °C the best-fit thermodynamic parameters for these equilibria were:

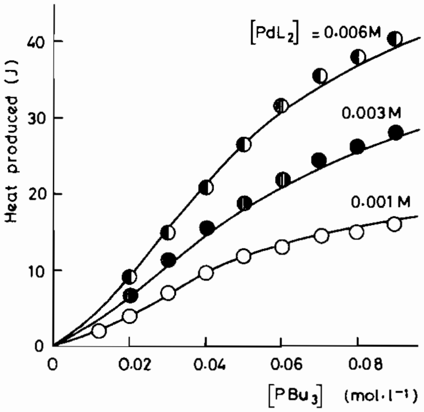

Figure 1. Calorimetric titration of PdL_2 with PBu_3 in acetonitrile solution at 30 °C. Total volume 100 ml.

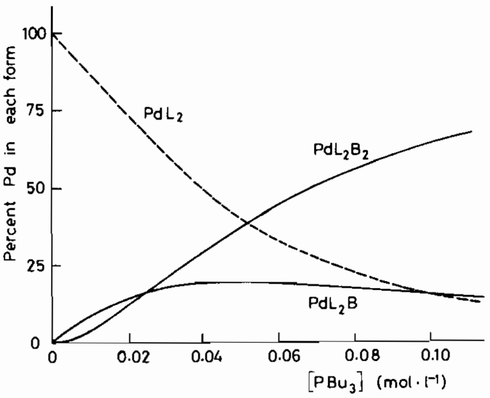

Figure 2. Concentrations of each species in equilibrium during titration of PdL_2 with PBu_3. Total concentration of Pd = 0.001 *M*.

$$PdL_2 + B \rightleftharpoons PdL_2B$$

$$K_1 = 10\ l\ mol^{-1},\ \Delta H_1^\circ = -53\ kJ\ mol^{-1}$$

$$PdL_2B + B \rightleftharpoons PdL_2B_2$$

$$K_2 = 40\ l\ mol^{-1},\ \Delta H_2^\circ = -53\ kJ\ mol^{-1}$$

where LH = methylethylglyoxime and B = PBu_3. The fit of experimental points to computed enthalpograms is shown in Fig. 1; Fig. 2 shows how the concentration of each species in equilibrium varies with increasing concentration of PBu_3.

When the PBu_3 concentration was considerably greater than that of the palladium compound it was observed that equilibrium was established only slowly, suggesting that under these conditions a more complex reaction occurs, involving bond breaking. The rate of evolution of heat after addition of a large excess of PBu_3 was found to follow first order

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kinetics; approximate rate constants, determined calorimetrically from reaction half times, were proportional to the PBu_3 concentrating, giving an overall rate equation:

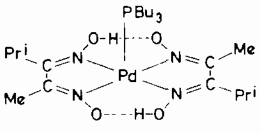
$$dQ/dt = k[PdL_2][PBu_3]$$

where Q is the heat evolved. Since in the accessible range of concentrations of PBu_3 ($10^{-2} < [PBu_3] < 10^{-1}$ *M*), the concentration of $PdL_2(PBu_3)_2$ is approximately proportional to that of PBu_3 (Fig. 2), this suggests a reaction mechanism in which the slow step is the dissociation of the 1:2 adduct $PdL_2(PBu_3)_2$:

$$PdL_2 \rightleftharpoons PdL_2(PBu_3) \rightleftharpoons PdL_2(PBu_3)_2 \rightarrow \text{products}$$

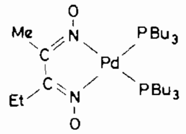
These conclusions are supported by the isolation of two different reaction products from solutions of PdL_2 and PBu_3 considerably more concentrated than those used in equilibrium or kinetic studies:

1) From solutions containing bis(methylisopropylglyoximato)palladium(II) and PBu_3 in the molar ratio 1:1 a crystalline product was obtained, shown by analysis to be the 1:1 adduct $PdL_2(PBu_3)$; the infrared spectrum of this compound in the O–H stretching region was identical with that of PdL_2, showing that the O–H···O bridges remain intact and the P atom must occupy an apical site in a 5-coordinate, square-pyramidal adduct (I).



I

2) From solutions containing bis(methylethylglyoximato)palladium(II) and 3–20-fold excess of PBu_3, on standing overnight, a solid product was obtained, shown by analysis to be $PdL(PBu_3)_2$. This compound was readily soluble in organic solvents and n.m.r. spectra in $CDCl_3$ confirmed the ratio 1:1:6 for the methyl:ethyl:butyl groups. It is evidently a 4-coordinate complex containing one, doubly deprotonated glyoximato group (II).



II

Experimental

Bis(glyoximato)palladium(II) complexes were prepared from an ethanolic solution of the glyoxime and $PdCl_2$ in 0.2*M* HCl solution. After filtration they were dried at 110 °C and purity checked by C, H, N and Pd analyses. PBu_3 was purified by redistillation under reduced pressure. Benzene for use in calorimetric experiments was redistilled and dried over calcium hydride. Calorimetric measurements were made on a LKB 8700 titration calorimeter by the previously described technique [5]; the method of analysis of titration curves for two simultaneous equilibria has also been described previously [6].

Acknowledgments

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