Base-catalyzed Conversion of π-Alkene–Palladium Chloride Complexes into π-Allyl Complexes

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SUBSTITUTED BIS-(π-ALLYLPALLADIUM CHLORIDES) have been prepared in low to moderate yields by heating the corresponding alkene–palladium chloride complexes above 60°.[1] This method is most effective for systems in which the olefin has the structure $R^1R^2C{=}CH_2$ so that the product is a 2-substituted bis-(π-allylpalladium chloride). A variation, which has proved effective for the preparation of very pure bis-(π-allylpalladium chlorides) containing substituted phenyl groups on the carbon-2, is to slowly add $PdCl_2(MeCN)_2$ to the olefin at 150—200°.[2]

The simplest alkene–palladium chloride π-complex that has been directly converted into the π-allyl complex by heating is that derived from isobutene.[3] It has been stated that the preparation of unsubstituted bis-(π-allylpalladium chloride) from the propene π-complex is not possible because the principle reaction, in this case, is the formation of acetone.[4] This, of course, can only be true in the presence of oxygen-containing compounds and, in the absence of air or moisture, the principal reaction is dimerization of the excess of propene and ultimately, formation of π-allyl complexes from the resulting hexenes.[5]

Recently, Morelli and his co-workers have shown that but-1-ene– and higher n-alkene–palladium chloride complexes are converted into the π-allyl complexes in 30—35% yield by addition of dimethyl formamide at room temperature.[6] The authors proposed that the initial step in this reaction involves the removal of a proton from the organic ligand by the dimethyl formamide. This prompts us to report our observation that several weak inorganic bases will catalyze the conversion of alkene–palladium chloride π-complexes into the π-allyl complexes at room temperature.

In a typical experiment, 2·0 g of di-μ-chlorodichlorobispropenedipalladium was stirred with 10·0 g of dried Na_2CO_3 in 25 ml. of ethanol-free chloroform for 5 hr. at 25°. The base was filtered and $CHCl_3$ pumped off. The residue was shown by n.m.r. spectra (d, τ 6·96, area 2·06; d, τ 5·90, area 2·05; m, τ 4·50, area 1·0) and i.r. spectra to be identical to an authentic sample of bis-(π-allylpalladium chloride). In the absence of Na_2CO_3, only the starting compound was recovered. The reaction is rapid at elevated temperatures; thus under reflux with $CHCl_3$, conversion is complete in 15 min.

By an identical procedure, di-μ-chlorodichlorobis(butene)dipalladium was converted to bis-(π-1-methylallylpalladium chloride) (n.m.r. spectrum: d, τ 8·67, area 3·08; d, τ 7·15, area 1·0; m, τ 4·67, area 0·98).

Other bases that were effective were $NaHCO_3$, Na_2HPO_4, and NaO_2CMe, the latter giving an acetate-bridged complex. The salts $CaCO_3$, $CaHPO_4$, and, surprisingly, Li_2CO_3 were completely ineffective. When K_2CO_3 was used, no π-allyl product was obtained but, instead, there was partial conversion to a new species which showed a multiplet from τ 8·8—9·2 in the n.m.r. spectra. We have not, as yet, identified this material.

It is not necessary to pre-form the π-complex of the alkene before treating with the base. Thus, when $PdCl_2$ (2 g.), Na_2CO_3 (10 g.), and 2-methylpent-1-ene (7 ml.) were stirred at room temperature for 5 hr. in 25 ml. of $CHCl_3$, a quantitative yield of bis-(2-n-propyl-π-allylpalladium chloride) was obtained.

The ease with which alkene π-complexes of $PdCl_2$ lose a proton to weak bases means that they are rather strong organic acids. There is evidence that this is true even for the ethylene complex. Thus, when di-μ-chlorodichlorobisethylenedipalladium is treated with Pr^iOH alone, ethylene is displaced from the complex and the major product is Pr^iCl.[7] However, when Na_2HPO_4, which can assist in the removal of a proton, is added the ethylene is attacked by the alcohol and di-isopropyl acetal is formed.[7,8]

We have attempted to confirm the report that some of these reactions are reversible, *i.e.* that HCl will react with π-allyl complexes to give the π-alkene species.[3] All such attempts have failed. In all cases we have only obtained materials having elemental analyses and n.m.r. spectra that could not be interpreted.

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