Palladium-mediated Transfer of Oxygen from Carbonate Ion to an Organic Ligand

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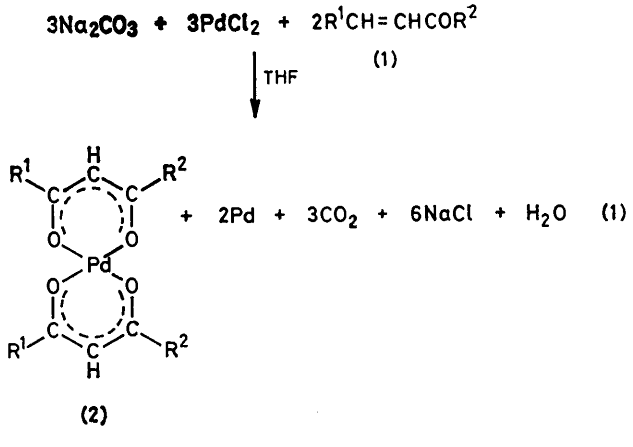
Summary Reaction of some $\alpha\beta$-unsaturated ketones with palladium(II) chloride and sodium carbonate in tetrahydrofuran (THF) gives acetylacetonate complexes; use of ^{18}O-enriched carbonate shows that the reaction involves a highly unusual transfer of oxygen from carbonate ion to the organic ligand.

We report what we believe is the first example of transfer of oxygen from carbonate ion to an organic ligand during formation of a metal complex. Reaction of a range of $\alpha\beta$-unsaturated ketones with palladium(II) chloride and sodium carbonate in tetrahydrofuran (THF) leads to the formation of acetylacetonate (Hacac) complexes. The reaction occurs with concurrent formation of palladium and results are consistent with equation (1).

Yields of acac complexes were in the range 40—70% when based on this equation for reactions in which palladium(II) was the limiting reagent. Yields of recovered palladium were in the region of 82—99%. Reactions were carried out in a nitrogen atmosphere using anhydrous, peroxide-free THF.



(2)

However, to eliminate the possibility that THF was donating the oxygen, a reaction was carried out using 40% ^{18}O-enriched sodium carbonate and pent-3-en-2-one. The resulting bis(acetylacetonato)palladium(II) (**2**; $R^1 = R^2 =$ Me) was shown to contain *ca.* 54% ^{18}O by comparison of the intensity of the mass spectral peak at *m/e* 302 due to $^{12}C_{10}{}^{1}H_{14}{}^{16}O_{4}{}^{104}Pd$ with that at *m/e* 304 principally due to $^{12}C_{10}{}^{1}H_{14}{}^{16}O_{4}{}^{106}Pd$ and $^{12}C_{10}{}^{1}H_{14}{}^{16}O_{3}{}^{18}O_{1}{}^{104}Pd$. Thus, more than two thirds of the available ^{18}O had been incorporated. An earlier reaction with ^{18}O-labelled carbonate gave the acac complex with variable yields of incorporation of about half the above levels.

When sodium carbonate was no longer included in the reaction mixture the acac compound was no longer formed but *e.g.* with phenyl prop-1-enyl ketone (**1**; R^1 = Me, R^2 = Ph) an acyl π-allyl palladium compound was formed instead. Good yields of substituted acac palladium complexes were formed from pent-1-enyl phenyl ketone (**1**; R^1 = Pr; R^2 = Ph) and phenyl prop-1-enyl ketone (**1**; R^1 = Me; R^2 = Ph), while chalcone (**1**; $R^1 = R^2$ = Ph) gave a modest yield (35%). The reaction was first discovered when a small amount of crystalline material from a reaction of pent-1-enyl phenyl ketone was separated by hand to give crystals of the *cis*- and *trans*-isomers of compound (**2**; R^1 = Pr, R^2 = Ph) whose structures were obtained by *X*-ray analysis.[1] No acac complex was formed from a reaction of 1-acetyl-4-t-butylcyclohexene, suggesting that the transition state leading to acac formation has significant steric requirements.

The mechanism of the reaction was shown not to involve oxidation of the enones with oxidants arising from interaction of sodium carbonate with sodium chloropalladate, for when a mixture of palladium(II) chloride, sodium chloride, and sodium carbonate was stirred for 14 h and the ketone then added no reaction of the enone occurred, other than a small amount of polymerisation. When palladium(II) oxide was prepared[2] and used in place of Pd^{II} chloride and sodium carbonate, again the enone was recovered together with a little polymeric material. The possibility that the carbonate oxygen was first converted into water which then reacted with enone was eliminated by two experiments. In the first, water (7 mmol) was added to a reaction mixture containing sodium carbonate and this resulted in a decreased yield of acac complex (18%). In the second experiment the sodium carbonate was omitted and water added, resulting in the formation of a π-allyl complex.

When calcium carbonate was used in place of sodium carbonate, the π-allyl complex was formed. The yields of acac complexes were decreased when potassium carbonate was used (15%) or when 18-crown-6 ether was added to a reaction mixture containing sodium carbonate (36%). An appreciable yield of acac complex was obtained using sodium hydrogen carbonate (54%) but none was formed when sodium hydroxide was used.

Reactions of the enone with sodium chloropalladate in ethanol showed similar trends although yields of organometallic products were lower. Reaction in the presence of sodium carbonate gave the acac compound (15%) and in the absence of sodium carbonate the π-allyl compound (20%).

We believe these experiments suggest that carbonate ion can attack an intermediate enone–palladium complex either by direct nucleophilic attack on the ligand or initially *via* complexation with the metal. An example has been discovered recently of a carbonate ion functioning as a nucleophile in the cobalt-catalysed hydrolysis of nitriles,[3] but otherwise carbonate oxygen has not been reported to transfer to an organic reactant. Transfer of oxygen from carbonate to metal ions, *e.g.* cobalt(III), has been shown to occur readily.[4] The palladium-catalysed transfer of oxygen from t-butylhydroperoxide to $\alpha\beta$-unsaturated ketones resulting in the formation of β-diketones has recently been reported.[5]

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