

Preliminary communication

REACTION OF CARBON DIOXIDE WITH A BIMETALLIC OCTADIENYL-BRIDGED PALLADIUM COMPLEX

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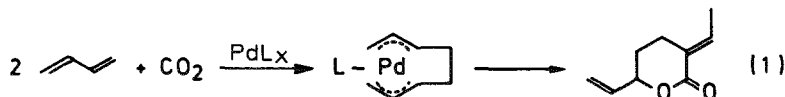
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Summary

Reaction of equimolar amounts of μ -1-3- η :6-8- η -octadienatobis(1,1,1,5,5,5-hexafluoroacetylacetonatopalladium) and triisopropylphosphine gives a bimetallic octadienyl-bridged complex, in which one palladium atom is η^1 -bound to the terminal carbon of the octadienyl chain. Insertion of CO_2 into this Pd—C bond gives a carboxylate complex; acidic decomposition and hydrogenation of the carboxylate complex gives pelargonic acid. The results are discussed in relation to the mechanism of the palladium-catalyzed reaction between butadiene and carbon dioxide.

Palladium and nickel complexes containing an α,ω -octadienyl chain are thought to be key intermediates in oligomerizations [1] and telomerizations [2]. Various mechanisms have been proposed in which both mono- and bimetallic complexes appear as catalytic intermediates. Some binuclear complexes containing a bridging octadienyl ligand which can serve as models for the catalytic active species have been prepared by treating a transition metal complex with butadiene: Green [3] isolated the complexes μ -(octadienyl)[NiBr(PPr₃)]₂ and μ -(octadienyl)-[NiX(dppe)]₂, and White [4] prepared the polymeric μ -(octadienyl)bis(chloropalladium) and the monomeric μ -(octadienyl)bis(cyclopentadienatopalladium).

Following our investigations of the palladium-catalyzed reaction between butadiene and carbon dioxide we proposed a mechanism involving a mono-nuclear palladium species [5]. In this mechanism a bis- η^3 -allylpalladium com-



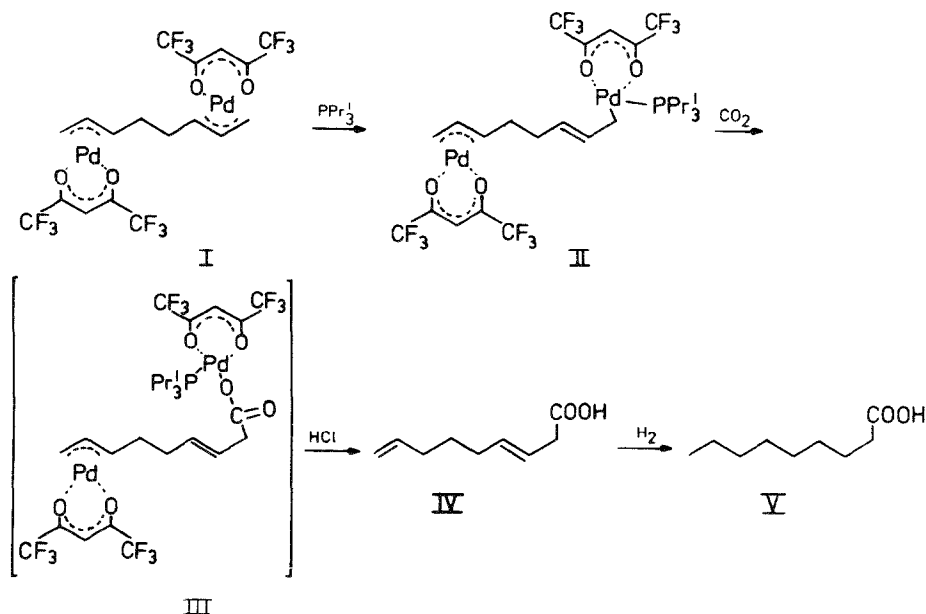
plex is assumed to be in equilibrium with the corresponding $\eta^1-\eta^3$ -intermediate. After insertion of carbon dioxide into the Pd—C bond of this intermediate a carboxylate complex is formed, and yields the δ -lactone-2-ethylidene-6-hepten-5-olide as the reaction product.

The question arose as to whether binuclear palladium complexes might also act as intermediates in the reaction of butadiene with CO_2 . In order to see whether the δ -lactone is in fact, formed by the reaction in presence of a bimetallic complex we studied the stoichiometric insertion reaction of carbon dioxide with a new binuclear μ -(octadienyl)palladium complex.

Results and discussion

Palladium bis(1,1,1,5,5,5-hexafluoroacetylacetonate) reacts with butadiene to yield complex I, the μ -1-3- η :6-8- η -octadienatobis(1,1,1,5,5,5-hexafluoroacetylacetonatopalladium) [6]. This complex can add one equivalent of triisopropylphosphine to yield selectively complex II, in which only one palladium metal is attacked by the ligand (Scheme 1). Complex II is a very suitable model compound for studying the mechanism of the reaction of butadiene and carbon dioxide, because we showed that the analogous "in situ" catalyst system formed by palladium bis(hexafluoroacetylacetonate) and triisopropylphosphine gave the δ -lactone 2-ethylidene-6-hepten-5-olide in 33% yield.

The reaction of complex II with carbon dioxide in acetonitrile yielded the carboxylate complex III, which was identified by its strong absorption in the infrared spectrum at 1635 cm^{-1} . The palladium complex III was not isolated, but further characterized by treatment with 2 *M* hydrochloric acid to give the 3,8-nonadienoic acid IV. After hydrogenation of acid IV with Raney-nickel as catalyst, pelargonic acid V was obtained in a 44% yield based on the amount of complex I initially taken.



The fact that the linear pelargonic acid, and not the branched δ -lactone, is formed in the reaction of the bimetallic octadienyl-bridged palladium complex with carbon dioxide indicates that the reaction of butadiene with carbon dioxide to give the δ -lactone goes by a mechanism different from that shown in Scheme 1. The formation of the linear acid can be attributed to the fact that in complex II one palladium atom is η^1 -bound to the octadienyl chain at the terminal carbon atom C(1) and not at the internal C(3) atom, as is fully confirmed by the ^1H NMR spectrum. The formation of pelargonic acid can be explained in terms of the insertion of carbon dioxide into the η^1 -palladium—carbon bond of a terminally-fixed octadienyl chain.

Insertions of CO_2 into transition metal—allyl bonds have been much studied [7], but insertion of carbon dioxide has previously been always found to occur in the C(3) position to give branched products, and not in the C(1) position [8,9]. The unusual binding of the octadienyl chain in complex II can be attributed to steric hindrance by the ligands. The bulk of the bridging octadienyl chain, of the chelate hexafluoroacetylacetonate ligand, and large triisopropylphosphine allow formation only of the unusual structure II.

Experimental

A solution of 0.25 g (0.34 mmol) of complex I and 0.054 g (0.34 mmol) of triisopropylphosphine in 10 ml of CH_3CN was transferred under argon to a 75 ml steel autoclave. Carbon dioxide was admitted up to a pressure of 60 atm, and the solution stirred at 65°C for 16 h; during the reaction the colour of the solution changed from brownish-yellow to deep-red. Subsequently 25 ml of 2 *M* aqueous HCl was added, and the palladium complex was decomposed by stirring at room temperature for 3 h. After neutralization with 2 *M* aqueous NaOH the acid IV was extracted with diethyl ether and the ethereal solution was dried (CaCl_2). After removal of the ether, 10 ml of a toluene suspension of Raney-nickel was added and hydrogenation carried out in a steel autoclave under 25 atm of H_2 at 60°C for 16 h. After filtration hexadecane was added as an internal standard and the sample analyzed by GLC (Carlo Erba 2300 S, 50m basic WG 11 capillary column, temperature program 100-230 $^\circ\text{C}$) and GLC/MS (Varian MAT 112 S).

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