

$\eta^1, \eta^3$ -Octadienediyl-palladium Complexes

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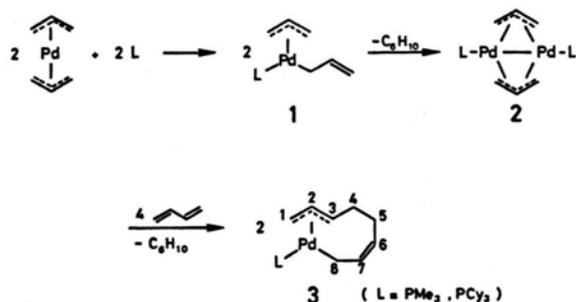
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D-4330 Mülheim an der RuhrZ. Naturforsch. **36b**, 1198–1199 (1981);  
received May 13/June 9, 1981Palladium- $\eta^3$ -allyl Complex

1,3-Dienes react with bis( $\eta^3$ -allyl)palladium-ligand systems to give the title compounds which are believed to be involved, as intermediates, in the palladium-catalyzed oligomerization of dienes.

$\eta^1, \eta^3$ -Octadienediyl-palladium complexes have been repeatedly postulated to be involved, as intermediates, in the palladium-catalyzed oligomerization, co-oligomerization and telomerization of 1,3-dienes [1]. Although the corresponding complexes of nickel [2] and platinum [3] have been isolated and, particularly in the case of nickel, investigated in some detail, systems involving palladium have not been previously reported.

We have now found that  $\eta^1, \eta^3$ -octadienediyl-palladium-trialkylphosphine complexes (3) can be easily prepared as stable, air-sensitive, yellow crystalline solids by reacting bis( $\eta^3$ -allyl)palladium with the phosphine and butadiene at, or near, room temperature in ether-butadiene (1:1) as solvent. The reaction presumably involves the binuclear complex 2 since we have already shown that bis( $\eta^3$ -allyl)palladium reacts, at low temperature, with donor ligands to give initially the adduct 1 [4, 5], in which one  $\eta^3$ -allyl group has adopted an  $\eta^1$ -allyl arrangement, which in turn disproportionates at 0 °C to give 2 [6, 7].

The structure of 3 has been confirmed by detailed NMR investigations ( $^{13}\text{C}$ - $\{^1\text{H}\}$ -NMR spectrum (25.2 MHz) of 3 (L =  $\text{PMe}_3$ ) at  $-30^\circ$  in d-toluene:  $\delta\text{C}_1$  56.3,  $\delta\text{C}_2$  115.8,  $\delta\text{C}_3$  68.0,  $\delta\text{C}_4$  25.3,  $\delta\text{C}_5$  25.9,

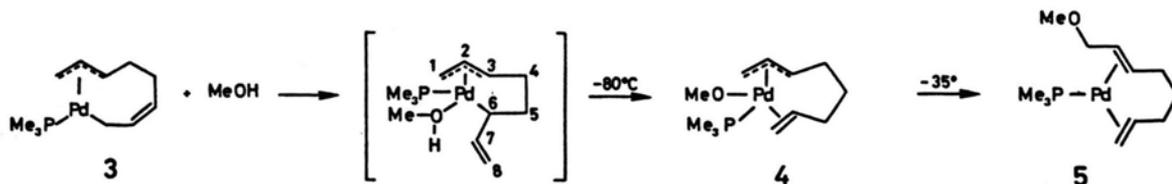


$\delta\text{C}_6$  106.2,  $\delta\text{C}_7$  133.2,  $\delta\text{C}_8$  11.6,  $\delta\text{C}_{\text{PMe}}$  17.1;  $J_{\text{PC}_1}$  1.4,  $J_{\text{PC}_2}$  3.4,  $J_{\text{PC}_3}$  30.8,  $J_{\text{PC}_4}$  5.2,  $J_{\text{PC}_5}$  3.6,  $J_{\text{PC}_6}$  1.0,  $J_{\text{PC}_7}$  10.5,  $J_{\text{PC}_8}$  25.1 Hz) as well as by an X-ray crystal structure determination of the trimethylphosphine adduct [8]. Analogous reactions with isoprene lead to a mixture of isomers which have been shown by NMR spectroscopy to have the constitution  $[\text{PdL}(\eta^1, \eta^3\text{-}2,6\text{-Me}_2\text{C}_8\text{H}_{10})]$  and  $[\text{PdL}(\eta^1, \eta^3\text{-}2,7\text{-Me}_2\text{C}_8\text{H}_{10})]$ ; similar behaviour has been observed for the analogous nickel complexes [10].

The  $\eta^1, \eta^3$ -octadienediyl group is displaced upon reaction with carbon monoxide. The reaction in toluene occurs at  $-30^\circ\text{C}$  and 1 mol CO/Pd is absorbed with the almost exclusive elimination of butadiene (80%). Cleavage of the  $\text{C}_3$ -chain has also been observed in the analogous reactions involving nickel [2].

An indication of the relevance of 3 to the catalysis is given by the reaction with methanol: protonolysis occurs at  $-80^\circ\text{C}$  to give the  $\eta^2, \eta^3$ -octadienediyl-palladium methoxide complex (4) [11] (and is presumably preceded by ligand-induced isomerization of the  $\text{C}_8$ -chain) which reacts further at  $-35^\circ\text{C}$  to give 5 [12] in which 1-methoxy-2,trans,7-octadiene (the product of the palladium-ligand catalyzed telomerization of butadiene with methanol [1, 13]) is bonded as an  $\eta^2, \eta^2$ -organic ligand to palladium.

Experiments with MeOD show that, as expected, deuteration occurs exclusively at  $\text{C}_6$ . Heteroalkenes, e.g. aldehydes, Schiff bases, isocyanate and  $\text{CO}_2$ , react with 3 with insertion into the Pd-C bond.



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- [8] **3** ( $L = \text{PMe}_3$ ) is isomorphous with the analogous platinum complex [3] and has a similar disorder. The structural parameters are comparable with those of the related nickel complex  $[\text{NiPCy}_3(\eta^1, \eta^3\text{-}2,6\text{-Me}_2\text{C}_8\text{H}_{10})]$  [9].
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- [11]  $^{13}\text{C}\text{-}\{^1\text{H}\}$ -NMR spectrum of **4** (25.2 MHz) at  $-80^\circ$  in d-toluene:  $\delta_{\text{C}_1/\text{C}_8}$  74.9/71.0,  $\delta_{\text{C}_2}$  116.2,  $\delta_{\text{C}_3}$  97.1,  $\delta_{\text{C}_4}$  33.3,  $\delta_{\text{C}_5}$  28.4,  $\delta_{\text{C}_6}$  27.5,  $\delta_{\text{C}_7}$  107.3,  $\delta_{\text{CPMe}}$  15.3,  $\delta_{\text{COMe}} \sim 49.0$ ;  $J_{\text{PC}_1}$  5.8,  $J_{\text{PC}_3}$  22.7,  $J_{\text{PC}_4}$  6.6,  $J_{\text{PMe}}$  28.7 Hz.
- [12]  $^{13}\text{C}\text{-}\{^1\text{H}\}$ -NMR spectrum of **5** (25.2 MHz) at  $0^\circ$  in d-toluene:  $\delta_{\text{C}_1}$  75.8,  $\delta_{\text{C}_2}$  67.2,  $\delta_{\text{C}_3}$  75.7,  $\delta_{\text{C}_4}$  33.1,  $\delta_{\text{C}_5}$  31.0,  $\delta_{\text{C}_6}$  32.6,  $\delta_{\text{C}_7}$  76.4,  $\delta_{\text{C}_8}$  54.6,  $\delta_{\text{CPMe}}$  18.4,  $\delta_{\text{COMe}}$  56.5;  $J_{\text{PC}_1}$  8.1,  $J_{\text{PC}_3}$  5.5,  $J_{\text{PC}_4}$  13.7,  $J_{\text{PC}_5}$  8.9,  $J_{\text{PC}_6}$  3.4,  $J_{\text{PC}_7}$  3.6,  $J_{\text{PC}_8}$  11.5,  $J_{\text{PC}_9}$  3.7,  $J_{\text{PMe}}$  16.9 Hz.
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