\(\eta^1,\eta^3\)-Octadienediyl-palladium Complexes


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Palladium-\(\eta^3\)-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 \(\eta^3\)-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 (\(^1^3^C-(^-H)-(H)-NMR spectrum (25.2 MHz) of 3 (L = PMe₃) at −30° in d-toluene: \(\delta\)C₁ 56.3, \(\delta\)C₂ 115.8, \(\delta\)C₃ 68.0, \(\delta\)C₄ 25.3, \(\delta\)C₅ 25.9, \(\delta\)C₆ 106.2, \(\delta\)C₇ 133.2, \(\delta\)C₈ 11.6, \(\delta\)C₉ 17.1; \(\delta\)C₇ 1.4, \(\delta\)C₈ 3.4, \(\delta\)C₉ 30.8, \(\delta\)C₈ 5.2, \(\delta\)C₉ 3.6, \(\delta\)C₈ 10.0, \(\delta\)C₉ 10.5, \(\delta\)C₈ 25.1 Hz) as well as by an X-ray crystal structure determination of the trimethylphosphine adduct [8]. Analogous reactions with isopropene lead to a mixture of isomers which have been shown by NMR spectroscopy to have the constitution \([\text{PdL}(\eta^1,\eta^3-2,6-Me₂C₈H₁₀)]\) and \([\text{PdL}(\eta^1,\eta^3-2,7-Me₂C₈H₁₀)]\): 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 °C and 1 mol CO/Pd is absorbed with the almost exclusive elimination of butadiene (80%). Cleavage of the \(\text{C₈}\)-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 °C to give the \(\eta^1,\eta^3\)-octadienediyl-palladium methoxide complex (4) [11] (and is presumably preceded by ligand-induced isomerization of the \(\text{C₈}\)-chain) which reacts further at −35 °C to give 5 [12] in which 1-methoxy-2,3,7-octadiene (the product of the palladium-ligand catalyzed telomerization of butadiene with methanol [1, 13]) is bonded as an \(\eta^2\)-organic ligand to palladium.

Experiments with MeOD show that, as expected, deuteration occurs exclusively at \(\text{C₈}\). Heteroalkenes, e.g. aldehydes, Schiff bases, isocyanate and CO₂, react with 3 with insertion into the Pd-C bond.

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[8] 3 (L = PMe3) 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 [NiPCy3(η5-C5H5)2] [9].


[11] 13C-{1H}-NMR spectrum of 4 (25.2 MHz) at −80° in d-toluene: δC=74.9/71.0, δC=116.2, δC=97.1, δC=33.3, δC=28.4, δC=27.5, δC=107.3, δCPMe=15.3, δCOMe ~49.0; JFC=5.8, JFC=22.7, JFC=6.6, JPM=28.7 Hz.

[12] 13C-{1H}-NMR spectrum of 5 (25.2 MHz) at 0° in d-toluene: δC=75.8, δC=67.2, δC=75.7, δC=33.1, δC=31.0, δC=32.6, δC=76.4, δC=54.6, δCPMe=18.4, δCOMe=66.5; JFC=8.1, JFC=5.5, JFC=13.7, JFC=8.9, JFC=3.4, JFC=3.6, JFC=11.5, JFC=3.7, JPM=16.9 Hz.