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OC3 A New Type of Trimeric Formally Zerovalent Palladium Complexes only Supported by Nitrogen Ligands

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Ar-BIAN (bis(arylimino)acenaphthene) Schiff bases have found wide application as ligands for both transition and main group metals because their rigid structure imparts the correct geometry for chelation and improves the stability of the compounds against hydrolysis and rupture of the central C-C bond. We have previously reported on the synthesis of the reduced form of the BIAN compounds, Ar-BIANH₂.^{1,2} We now report that treatment of palladium acetate with these ligands results in the reduction of palladium(II) to palladium(0) and coordination of the so formed Ar-BIAN to the latter. In the absence of other ligands, an unprecedented trinuclear complex was obtained, which is formally the first palladium(0) compound only stabilized by nitrogen ligands. Its X-ray structure shows that each palladium atom is coordinated in a standard $\kappa^2\text{N}$ chelating way to an Ar-BIAN ligand and in a η^2 way to a C=N double bond of another Ar-BIAN ligand. The latter is itself chelating a second palladium atom and the same bonding scheme extend to a third Pd(Ar-BIAN) unit, which closes the loop over the first palladium atom (Figure 1).

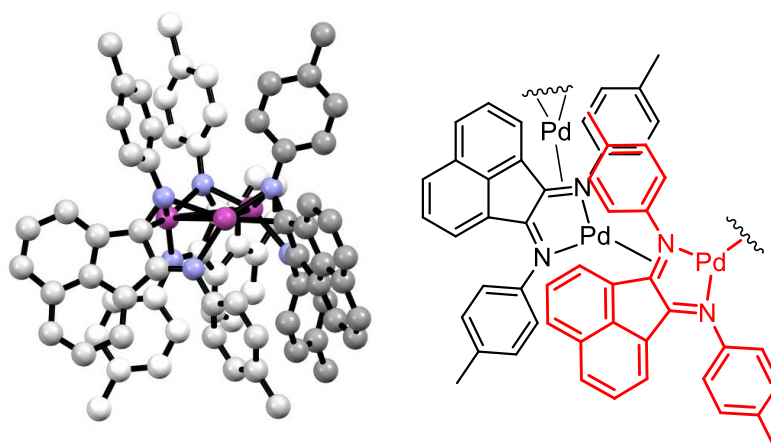


Figure 1 X-Ray structure of trimeric [Pd(4-MeC₆H₄-BIAN)]₃ and its partial bonding scheme.

Overall, the complex has a propeller shape, with the six aryl rings divided in two inequivalent groups. Other complexes have also been obtained showing unusual structures and their synthesis will be described.

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