Oxidative Dimerization of (P-P)Pt(SR)$_2$ to (P-P)Pt(μ-SR)$_2$Pt(P-P)

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(dppx)Pt(SEtOH)$_2$ complexes (dppx = 1,1’-bis(diphenylphosphino)ferrocene (dppf) or 1,2-bis(diphenylphosphino)ethane (dppe)) undergo oxidative dimerization reaction with the oxidizing reagent (TCNQ or TCNQF4). According to mass spectroscopic and electrochemical analysis, [(dppx)Pt(SEtOH)]$^+$ species are dimerized, affording dicaticonic bimetallic complexes formulated as [(dppx)Pt(μ-SEtOH)$_2$Pt(dppx)]$^{2+}$. The crystal structure analysis of [(dppe)Pt(μ-SEtOH)$_2$Pt(dppe)]TCNQF4$_2$ shows TCNQF4 radical anions ($g = 2.004$, $ΔB_{pp} = 18$G) are not coupled in the solid state structure. This molecular arrangement is compared with that of [(P2)Pt(μ-SA_r)$_2$Pt(P2)][TCNQF4]$_2$ (SA_r = benzenethiolate or 3,5-dimethylbenzenethiolate; P2 = 3,4-dimethyl-3’,4’-bis(diphenylphosphino)tetrathiafulvalene) in which the coupled TCNQF4 radical anions show a weak antiferromagnetic behavior. [1]

The bimetallic complexes with hetero- or homo-ligand pairs (dppf and dppe) can be prepared by metathesis, and compared with those prepared by oxidative dimerization method. (NRF 2010-0011478)