Carboxylatodirhodium(II) complexes with orthometallated tris(*p*-methoxyphenyl)phosphine and their reactions with pyrazole and imidazole.

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Streszczenie

Exchange reactions of the acetato bridges in [cis-Rh2(l-OAc)2{l-(C6H3-4-OMe)P(C6H4-4-OMe)2}2(HOAc)2]([1(HOAc)2]) fortrifluoroacetato and propionato bridges give new dirhodium(II) complexes with two orthometallated molecules of tris(p-methoxy-phenyl)phosphine (PMP): [cis-Rh2(l-O2CCF3)2{l-(C6H3-4-OMe)P(C6H4-4-OMe)2}2(HO2CCF3)2]([2(HO2CCF3)2]) and [cis-Rh2-(l-O2CCH2CH3)2{l-(C6H3-4-OMe)P(C6H4-4-OMe)2}2(HO2CCH2CH3)2]ÆHO2CCH2CH3([3(HO2CEt)2]ÆHO2CE respectively. X-raystructures of the complexes [2(H2O)(PrOH)]ÆPrOH and [3(HO2CEt)2]ÆHO2CEt, as well as of pyrazole adducts [2(C3H4N2)2] and[3(C3H4N2)2] have been determined. The Rh–Rh distances in [2(C3H4N2)2] and [3(C3H4N2)2] are a little longer than those in[2(H2O)(PrOH)]ÆPrOH and [3(HO2CEt)2]ÆHO2CEt. Reactions of all these complexes with pyrazole and imidazole were investigatedusing UV–Vis spectroscopy. It has been found that pyrazole molecules are coordinated to [1], [2] and [3] complexes more strongly thanimidazole. Reactions with pyrazole were also studied using NMR spectroscopy.Ó2006 Elsevier Ltd. All rights reserved.Keywords:Dirhodium(II) complexes; Functionalized phosphines; Pyrazole; Imidazole; Orthometallation1. IntroductionChemistry of dirhodium(II) complexes with phosphineshas been intensively studied since the discovery of the prod-uct of the reaction of rhodium tetraacetate with triphenyl-phosphine – one of the first examples of a bimetallicorthometallated compound[1]:[cis-Rh2(l-OAc)2{l-(C6H4)-PPh2}2(HOAc)2]. Great attention has been paid to differentorthometallated dirhodium(II) compounds with triaryl andalkyl-aryl phosphines because of the growing interest in theproblem of activation of the C–H bond[2–21]. Dirho-dium(II) acetato complexes with orthometallated phos-phines belong to the group of very efficient cytostaticagents[21].It has been proven that electrochemical properties andcatalytic activity of dirhodium(II) carboxylato complexesin carbene transfer reactions depend not only on the ortho-metallated phosphine, but also on the carboxylato bridges[3,10,16]. Antitumour activity of Rh2(l-O2CR)4complexesalso strongly depend on the R substituent[22].In

this work, we present the results of investigations onthe interactions of the [cis-Rh2(l-OAc)2{l-(C6H3-4-OMe)P(C6H4-4-OMe)2}2(HOAc)2]([1(HOAc)2]), [cis-Rh2(l-O2CCF3)2{l-(C6H3-4-OMe)P(C6H4-4-OMe)2}2]([2(HO2CCF3)2]) and [cis-Rh2(l-O2CCH2CH3)2{l-(C6H3-4-OMe)P(C6H4-4-OMe)2}2] ([3(HO2CEt)2]ÆHO2CEt)complexes with pyrazole (Hpz) and imidazole (Him) inorder to establish the influence of the different substituentsof the carboxylato bridges on the reactivity of these com-plexes in the reactions of the formation of adducts witharomatic nitrogen-donor ligands

Słowa kluczowe

Dirhodium(II) complexes, Functionalized phosphines, Pyrazole, Imidazole, Orthometallation1

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