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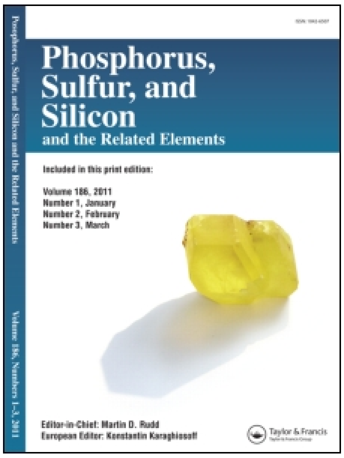

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Multinuclear NMR Study of Cationic Binuclear Mono- and Trihydrido Platinum (II) Bisphosphine Complexes

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MULTINUCLEAR NMR STUDY OF CATIONIC BINUCLEAR MONO- AND TRIHYDRIDO PLATINUM (II) BISPHOSPHINE COMPLEXES

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Abstract Magnitude and signs of J(Pt,Pt), J(Pt,P), J(Pt,H) and J(P,P) scalar couplings and hydride T_1 relaxation values characteristic for chelating systems are discussed.

Earlier reports on dinuclear platinum complexes involving **dppm** as bridging bidentate phosphine ligand suggested correlations that may exists between the magnitude and sign of the ^{2}J(Pt-P) and/or ^{3}J(Pt-P) coupling constant and the strength of the Pt-Pt bond [1]. In the case of cationic electron-deficient complexes where a hydrogen atom bridges the two metals the direct Pt-Pt bonding is expected to be rather weak, if any.

Bisphosphines with biting angle larger than that of **dppm** form chelates rings of different sizes rather then bridge between the Pt atoms. By systematic changing the biting distance of the chelating bisphosphines used (**dppe, chiraphos, dppp and bdpp**) we were looking for such correlations between the strength of the Pt-Pt interaction and the Pt-Pt coupling constants. The interesting Pt-Pt constants were obtained from the spin-simulation of the ^{31}P NMR spectrum of the relevant isotopomer. Magnitude and sign of the relevant Pt-P and P-P coupling values were determined from 1D ^{31}P and 2D P,P-COSY spectra.

The data obtained cast doubt on the existence of direct Pt-Pt bonding, but no unambiguous correlation could be obtained. Regardless of the chelate ring size the trihydrides studied all exhibit similar spectral features and show fluxional behaviour in agreement with earlier reports [2]. The temperature dependence of the hydride T_1 relaxation times of the different isotopomers confirms the low barrier of the exchange.

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