

Two-dimensional NMR studies of allyl palladium complexes of diphosphazanes

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h^3 -Allyl complexes are intermediates in organic synthetic reactions such as allylic alkylation and amination. There is growing interest in understanding the structures of chiral h^3 -allyl intermediates as this would help to unravel the mechanism of enantioselective C–C bond forming reactions. Two-dimensional NMR study is a powerful tool to elucidate the structures of such complexes. Here we present the synthesis of 1,3-diphenylallyl complexes of diphosphazanes of the type $X_2PN(R)PY_2$ and the monosulphide $Ph_2PN(CHMe_2)P(S)Ph_2$. NMR studies show the presence of only one isomer (e.g. A or B) in solution except for those diphosphazanes bearing C_2 -symmetric binaphthylendioxy moiety, in which case two isomers are observed (e.g. C and D). Allylic arrangement in these complexes has been determined by 2-D NOESY and ROESY spectra. These complexes are found to be active for C–C bond formation when they are treated with the sodium salt of dimethylmalonate.

