

^1H and ^{19}F PGSE diffusion and HOESY NMR studies on cationic palladium (II) 1,3-diphenylallyl complexes in THF solution

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THF solutions of the cationic chiral 1,3-diphenylallyl bidentate phosphine complexes $[\text{Pd}(\eta^3\text{-PhCHCHCHPh})(\text{Duphos})](\text{CF}_3\text{SO}_3)$, Duphos = 1,2-Bis-((2R,5R)-2,5-dimethylphospholano)benzene), **2**, and $[\text{Pd}(\eta^3\text{-PhCHCHCHPh})(\text{P,S})]\text{BF}_4$, **4**, P,S = [8-((*o*-(diphenylphosphino)benzyl) thiomethyl) – (7,7'-dimethyl)-*exo*-norborneol, have been studied via pulsed gradient spin-echo (PGSE) diffusion, ^1H , ^{19}F HOESY and a variety of other multi-dimensional NMR methods. On the basis of the ^1H , ^{19}F HOESY data, the anions show a preference for a specific structural position with respect to the $\eta^3\text{-PhCHCHCHPh}$ allyl ligand, i.e. the anion does not move evenly around the periphery of the cation. THF is shown to promote significant ion pairing, although neither **2** nor **4** shows 100% ion pairing. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^1H NMR; ^{19}F NMR; HOESY; PGSE diffusion; palladium allyl; cationic complexes; ion pairing in THF

INTRODUCTION

There is a substantial interest in the chemistry of allyl complexes of Pd (II) and especially in those molecules that contain chiral auxiliaries.¹ Further, there are now a number of known complexes, which catalyse the enantioselective allylic alkylation reaction and afford high chemical yield and excellent enantioselectivity.²

The recent catalytic literature has suggested that the nature of the anion can sometimes affect catalytic reaction kinetics.^{3–6} There are reports involving Ir-catalysed hydrogenation,³ Ru-catalysed Diels–Alder chemistry⁴ and Rh-catalysed addition of phenyl boronic acids to aldehydes,⁵ amongst others. Although these examples do not involve palladium, there is some interest in how anions interact with Pd–allyl complexes in connection with the so-called memory effects.^{7,8} This discussion revolves around whether a leaving group ‘remembers’ which carbon it came from, in an oxidative addition reaction, i.e. a form of anion effect.

Pulsed gradient spin-echo (PGSE) NMR diffusion methods⁹ are now currently widely used,^{10–16} and specifically, in connection with ion pairing. Several groups^{17–19} have now shown that PGSE measurements, in combination with ^1H , ^{19}F HOESY methods, offer a novel view of how the cations and anions of transition metal salts interact in solution. Further, the measured solvent dependencies^{20–22} of the diffusion constants, D , offer a hint as to the extent to

which any one solvent promotes ion pairing. It is now recognized that a variety of organic and inorganic salts dissolved in chloroform often lead to >95% ion pairing,²⁰ whereas the use of dichloromethane affords much less ion pairing. As in previous studies, it is assumed that when the cation and anion reveal nearly identical D -values, whose magnitudes afford hydrodynamic radii, r_{H} , values

$$r_{\text{H}} = kT/6\pi\eta D \quad (1)$$

D = Diffusion constant and η = viscosity

(via the Stokes–Einstein relation, Eqn (1)), which are substantially greater than those estimated either by crystallography or calculations, then we are dealing with about 100% ion pairing. Admittedly, the calculated r_{H} values assume spherical shapes, and this is rarely a reasonable assumption. Moreover, the value ‘6’, in the denominator of the equation, has been criticized.²³ Nevertheless, measured PGSE data for the individual ions offer a rapid, facile method of recognizing ion pairing.

To learn more about how ions interact, and, specifically, to determine whether there might be a preferred salt structure in chiral palladium species, we have measured ^1H , ^{19}F PGSE; ^1H , ^{19}F HOESY and a variety of other 2-D NMR spectra for two known cationic, palladium 1,3-diphenylallyl complexes, **2**²⁴ and **4**.²⁵ These salts are derived from the bidentate ligands **1** and **3** (see Scheme 1) and represent known allylation intermediates. We have chosen to measure in THF as we have recently shown²⁶ that, for $\text{Li}(\text{BF}_4)$, $(n\text{-Bu}_4\text{N})(\text{BF}_4)$, a tri-nuclear Ru (*p*-cymene) cluster and $[\text{Ir}(1,5\text{-COD})(\mathbf{5})](\text{BF}_4)$, where **5** is the chiral P, N ligand

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