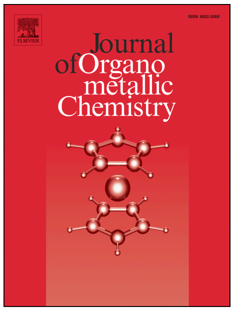

# A magnetic spin transfer NMR study of tertiary phosphine exchange in rhodium(I) complexes

Gertruida J.S. Venter

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# A magnetic spin transfer NMR study of tertiary phosphine exchange in rhodium(I) complexes.

*Gertruida J.S. Venter.*

Department Chemistry, University of the Free State, Bloemfontein 9300, South Africa. E-mail: VenterGJS@ufs.ac.za. Phone: +27(0)514019898; fax: +27(0)514017295.

**Keywords**

Magnetic spin transfer; exchange mechanism; kinetics; enaminoketone; rhodium; triphenylphosphine.

## Abstract

Magnetic spin transfer NMR was used to investigate phosphine exchange reactions in complexes of the type [Rh(N,O-Bid)(CO)($PPh_3$)] (where N,O-Bid is a derivative of 4-(phenylamino)pent-3-en-2-onate, Phony$^-$). Chlorido and methyl substituted rhodium phenyl β-enaminoketonato complexes, [Rh(2,6-$Cl_2$-Phony)(CO)($PPh_3$)] and [Rh(2,6-$Me_2$-Phony)(CO)($PPh_3$)], were chosen as study subjects allowing for a comparison of the influence of electronic properties on the rate of exchange. Moreover, a non-coordinating solvent, dichloromethane, was employed to minimize the effect of the solvent pathway. The rate of $PPh_3$ exchange in [Rh(2,6-$Cl_2$-Phony)(CO)($PPh_3$)] ($k_1$ = 218±16 $M^{-1}.s^{-1}$) was found to be approximately three times faster than the rate of reaction for the methylated counterpart ($k_1$ = 82±7 $M^{-1}.s^{-1}$). The methyl substituents increase the electron density of the *d*-orbitals of the rhodium atom and stabilize the five-coordinate distorted pyramidal intermediate, while the opposite is true for the complex with the chlorido-containing ligand. The activation parameters of the exchange reactions of both complexes correlate well with one another and an associative mechanism is indicated by the negative values for the entropy of activation, $\Delta S^{\ddagger}$, -117±9 and -124±12 $J.K^{-1}.mol^{-1}$. The activation process is primarily controlled by entropy as opposed to enthalpy (58 % and 61 % at 25°C for the respective complexes) and involves the formation of a stable, well-ordered transition state while bond weakening is less important.