Regio- and Stereo-selectivity in the Hydrogenation of Aryl Phosphines by Niobium Aryloxide Compounds

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The sequential hydrogenation of the three aryl rings in PPh_3 by the catalyst system $[Nb(OC_6HPh_4\text{-}2,3,5,6)_3Cl_2]/3Bu^nLi$ occurs with relative rates of 39:28:1; NMR analysis of the $PhPCy_2$ obtained from $[P(C_6D_5)_3/H_2]$ and $[P(C_6H_5)_3/D_2]$ shows a predominately all *cis* hydrogenation of both aryl rings has occurred.

The recently demonstrated ability of niobium aryloxide compounds to carry out the hydrogenation of aryl phosphines raises many mechanistic problems.[1,2] Two key questions concern substrate selectivity and the stereochemistry of the reaction. Aspects of both of these questions are addressed here.

Although originally demonstrated using the catalyst precursor $[Nb(OC_6H_3Ph_2\text{-}2,6)_2(CH_2C_6H_4\text{-}4Me)_3]$ ($OC_6H_3Ph_2$-2,6 = 2,6-diphenylphenoxide)[1] the hydrogenation of aryl phosphines can also be achieved in the presence of chloroaryloxides $[Nb(OAr)_2Cl_3]$ and $[Nb(OAr)_3Cl_2]$ (OAr = various 2,6-disubstituted phenoxides)[3] activated with varying ratios of Bu^nLi.† Monitoring (^{31}P NMR of aliquots‡) the hydrogenation of PPh_3 by the mixture $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3]/4Bu^nLi$ ($OC_6H_3Pr^i_2$-2,6 = 2,6-diisopropylphenoxide) over time (Fig. 1) shows that the third phenyl ring is hydrogenated at a much slower rate than the first two. The reaction profile can be fit using a consecutive first order kinetic model which yields the relative rates of hydrogenation of PPh_3, PPh_2Cy and $PPhCy_2$ (Fig. 1). The reaction profile at 60 °C is insensitive to the ratio of catalyst/substrate. In contrast, using bis(diphenylphosphino)methane (dppm) as substrate with the catalyst system $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_3Cl_2]/3Bu^nLi$ shows a completely different reaction profile (not yet modelled) in which the final product (dcpm) is generated with only small amounts of intermediates being built up (Fig. 2). This profile is possibly indicative of multiple arene rings being hydrogenated while the substrate is attached to a single catalyst site.

The catalyst mixture $[NbOC_6HPh_4\text{-}2,3,5,6)_3Cl_2]/3Bu^nLi$ containing 2,3,5,6-tetraphenylphenoxide ancillary ligation generates a reaction profile for PPh_3 in which the intermediate $PPhCy_2$ builds up dramatically (Fig. 3). This system can be used to synthetically prepare and purify $PPhCy_2$ whose ^1H NMR spectrum (assigned by a combination of COSY and HETCOR experiments) shows all eleven, non-equivalent cyclohexyl ring protons (Fig. 4). The samples of $PPhCy_2$ obtained by reacting $P(C_6H_5)_3$ with D_2 and $P(C_6D_5)_3$ with H_2 give ^1H NMR spectra consistent with a predominantly all *cis* hydrogenation of the two phenyl rings (Fig. 4). Mass spectrometric studies show that these samples are $[^2H_{12}]$ and $[^2H_{15}]$ respectively, *i.e.* negligible H/D [^2H] scrambling occurs during hydrogenation.

The hydrogenation of $MePPh_2$ by $[Nb(OC_6HPh_4\text{-}2,3,5,6)_3Cl_2]/3Bu^nLi$ proceeds *via* intermediate MePPhCy with

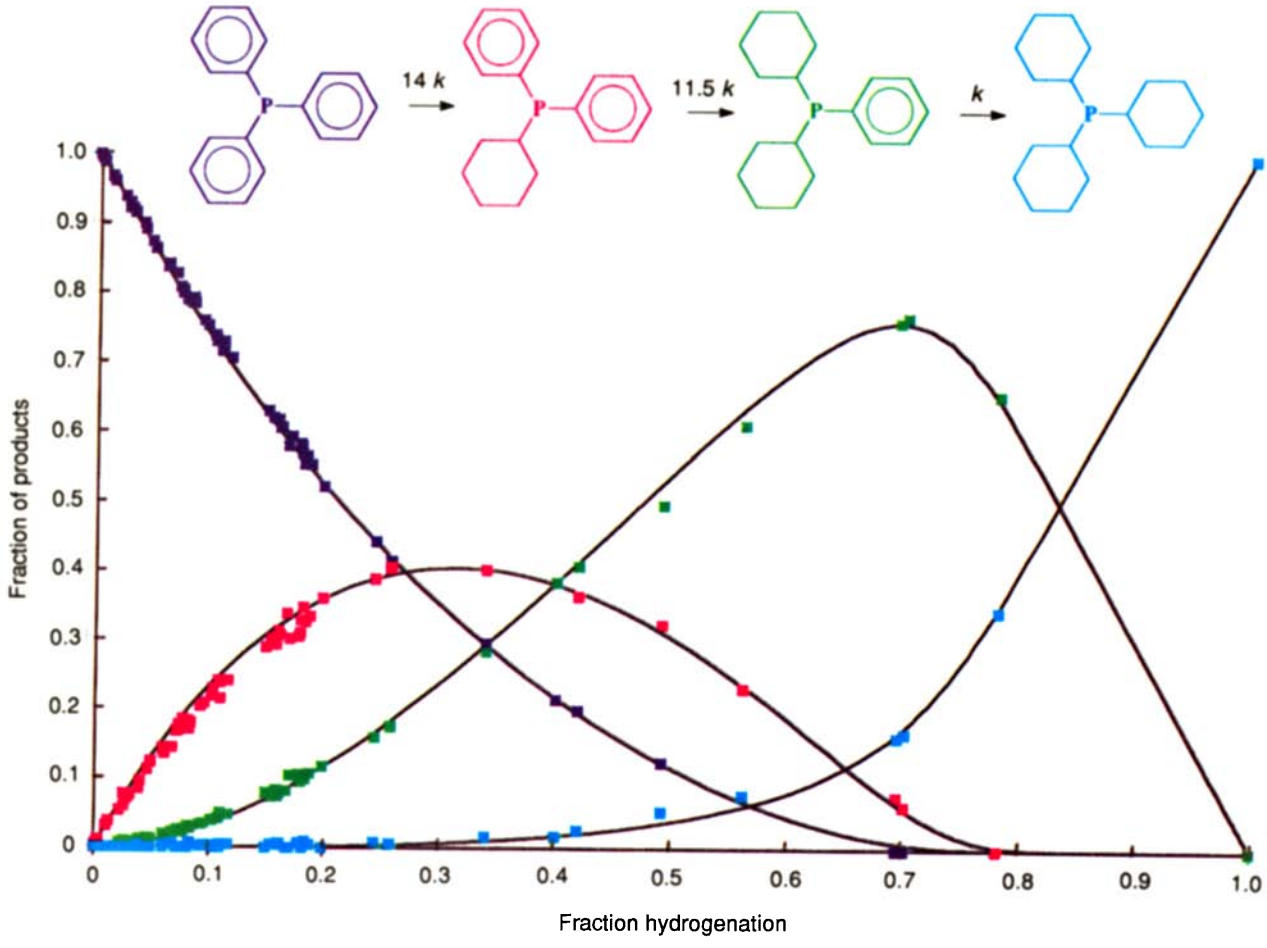

Fig. 1 Reaction profile (fraction of products *vs.* the fraction hydrogenation) for the hydrogenation of PPh_3 by the mixture $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3]/4Bu^nLi$ ($OC_6H_3Pr^i_2$-2,6 = 2,6-diisopropylphenoxide). The solid black lines represent the reaction profile predicted by the kinetic model shown.

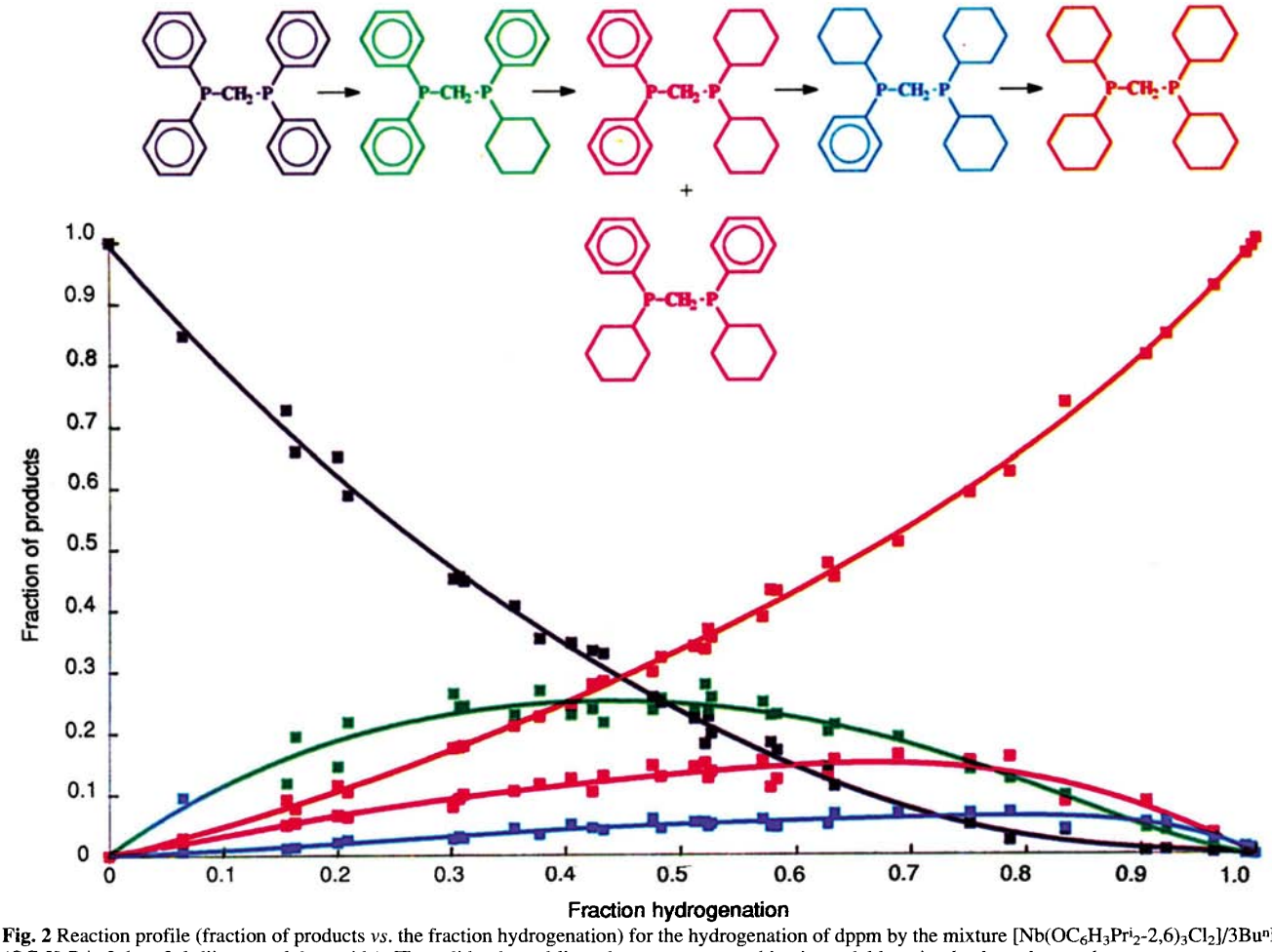

Fig. 2 Reaction profile (fraction of products *vs.* the fraction hydrogenation) for the hydrogenation of dppm by the mixture [Nb($OC_6H_3Pr^i_2$-2,6)$_3Cl_2$]/3Bu^{n}Li ($OC_6H_3Pr^i_2$-2,6 = 2,6-diisopropylphenoxide). The solid coloured lines do not represent a kinetic model but simply show the trends.

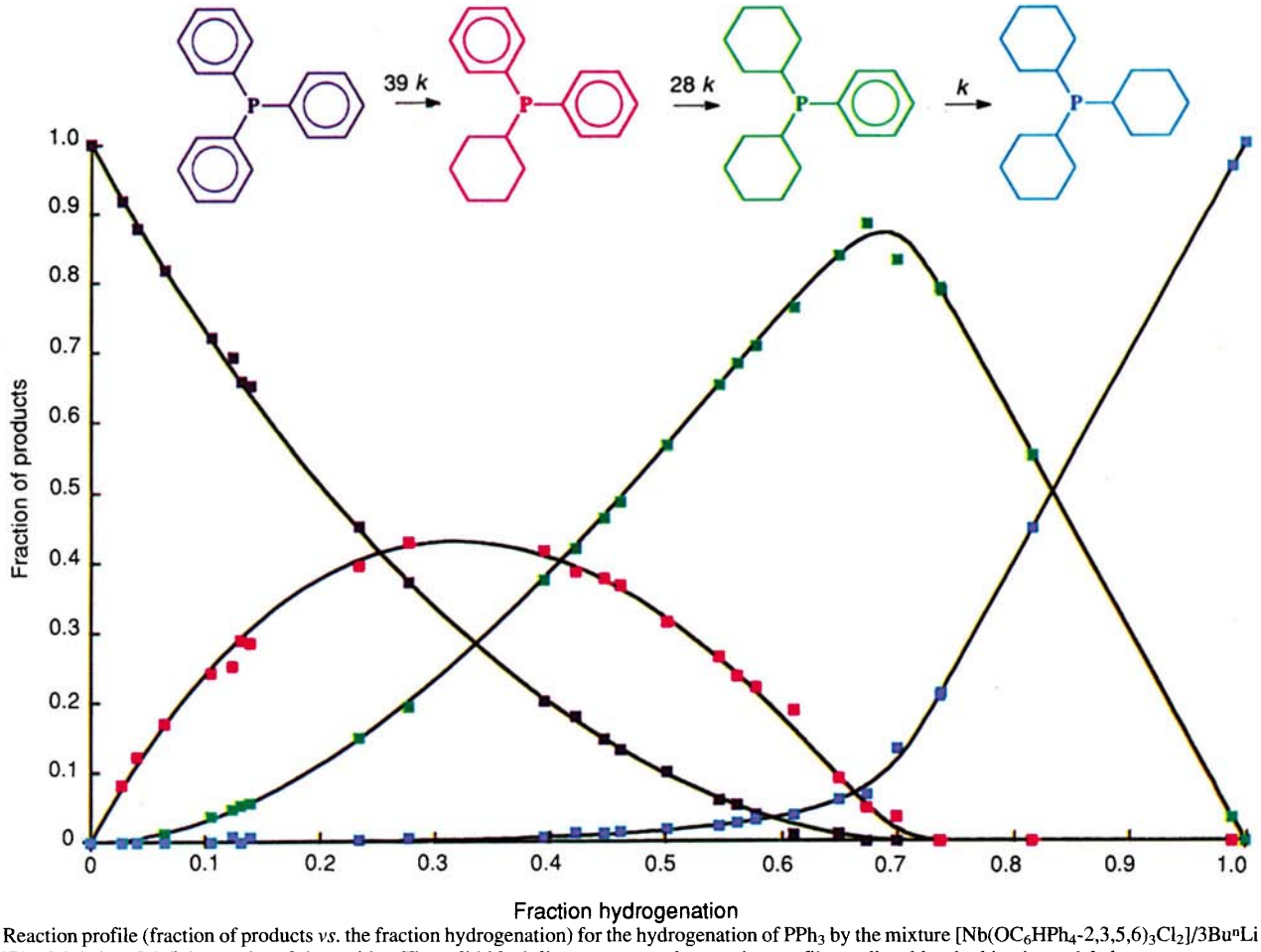

Fig. 3 Reaction profile (fraction of products *vs.* the fraction hydrogenation) for the hydrogenation of PPh_3 by the mixture [Nb(OC_6HPh_4-2,3,5,6)$_3Cl_2$]/3Bu^{n}Li (OC_6HPh_4-2,3,5,6 = 2,3,5,6-tetraphenylphenoxide). The solid black lines represent the reaction profile predicted by the kinetic model shown.

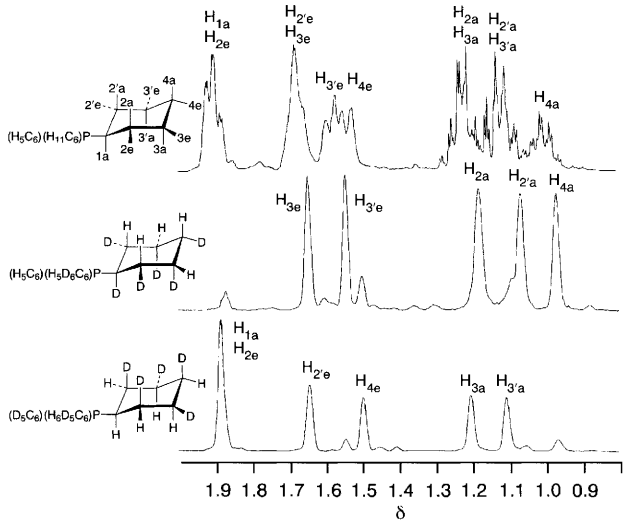

Fig. 4 ^{1}H NMR spectra of the aliphatic region (500 MHz, C_6D_6, 30 °C) for $P(C_6H_5)(C_6H_{11})_2$, $P(C_6H_5)(C_6H_5D_6)_2$ and $P(C_6D_5)(C_6D_5H_6)_2$ obtained using the mixture $[Nb(OC_6HPh_4\text{-}2,3,5,6)_3Cl_2]/3Bu^nLi$ (OC_6HPh_4-2,3,5,6 = 2,3,5,6-tetraphenylphenoxide) to carry out the reactions $[P(C_6H_5)_3/H_2]$, $[P(C_6H_5)_3/D_2]$ and $[P(C_6D_5)_3/H_2]$

a reaction profile modelled by a 2 : 1 ratio of rate constants, *i.e.* $MePPh_2$ is hydrogenated twice as fast as MePPhCy. The bulkier Pr^iPPh_2, however, generates the chiral (unresolved) intermediate Pr^iPPhCy in > 80% isolable yield (rate constant ratio of *ca.* 28 : 1). ^{1}H NMR of the $Pr^iPPh(C_6H_5D_6)$ obtained by reacting Pr^iPPh_2 with D_2 again shows a predominantly all *cis* arene hydrogenation has occurred (Fig. 5).

We thank the Department of Energy for support of this research.

Received, 9th December 1994; Com. 4/07536F

Footnotes

† In a typical procedure, a 300 ml stainless steel high pressure reactor fitted with a glass liner was charged in a dry box with $[Nb(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_3]$ (0.26 g, 0.47 mmol) and PPh_3 (2.5 g, 9.5 mmol) in benzene (17 ml). After the addition of Bu^nLi in hexane (3.0 ml of 0.5 mol l^{-1}, 1.5 mmol), the reactor was pressurized with H_2 (1200 psi initial pressure) and heated at 60 °C for varying amounts of time.

‡ *Selected data*: ^{31}P NMR (C_6D_6, 30 °C): for $P(C_6H_5)_3$, δ −4.93; $P(C_6D_5)_3$, −5.60; $P(C_6H_5)_2(C_6H_{11})$, −3.55; $P(C_6H_5)_2(C_6H_5D_6)$, −3.85; $P(C_6D_5)_2(C_6D_5H_6)$, −4.00; $P(C_6H_5)(C_6H_{11})_2$, 2.45; $P(C_6H_5)(C_6H_5D_6)_2$, 1.83; $P(C_6D_5)(C_6D_5H_6)_2$, 2.02; $P(C_6H_{11})_3$, 10.27; $P(C_6H_5D_6)_3$, 9.15; $P(C_6D_5H_6)_3$, 10.00; $P(Pr^i)(C_6H_5)_2$, 1.09; $P(Pr^i)(C_6H_5)(C_6H_{11})$, 6.65; $P(Pr^i)(C_6H_5)(C_6H_5D_6)$, 6.31; $P(Pr^i)(C_6H_{11})_2$, 13.71; $P(Pr^i)(C_6H_5D_6)_2$, 12.97.

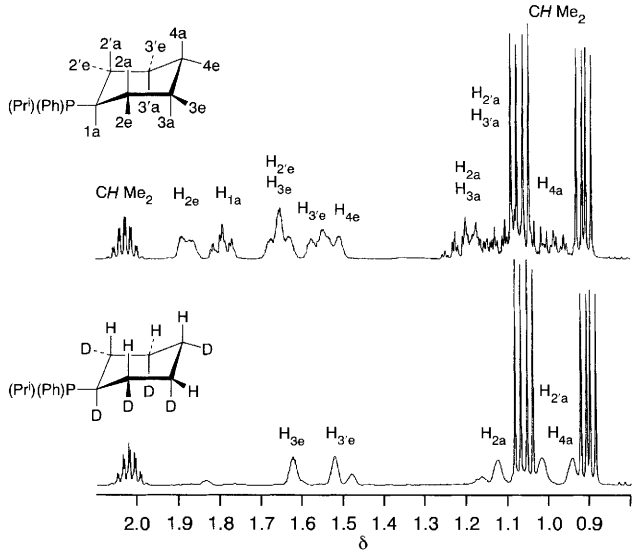

Fig. 5 ^{1}H NMR spectra of the aliphatic region (500 MHz, C_6D_6, 30 °C) for $P(Pr^i)(C_6H_5)(C_6H_{11})$ and $P(Pr^i)(C_6H_5)(C_6H_5D_6)$ obtained using the mixture $[Nb(OC_6HPh_4\text{-}2,3,5,6)_3Cl_2]/3Bu^nLi$ (OC_6HPh_4-2,3,5,6 = 2,3,5,6-tetraphenylphenoxide) to carry out the reactions $[P(Pr^i)(C_6H_5)_2/H_2]$ and $[P(Pr^i)(C_6H_5)_2/D_2]$

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