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 PPh₃ by the catalyst system [Nb(OC₆HPh₄-2,3,5,6)₃Cl₂]/3BuⁿLi occurs with relative rates of 39:28:1; NMR analysis of the PhPCy₂ obtained from [P(C₆D₅)₃/H₂] and [P(C₆H₅)₃/D₂] 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 $[Nb(OC_6H_3Ph_2-2,6)_2(CH_2C_6H_4-4Me)_3]$ (OC₆H₃Ph₂-2,6 = 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 BunLi.⁺ Monitoring (³¹P NMR of aliquots[‡]) the hydrogenation of PPh₃ by the mixture [Nb(OC₆H₃Pri₂-2,6)₂Cl₃]/4BuⁿLi (OC₆H₃Pri₂-2,6 = 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 PPh₃, PPh₂Cy and PPhCy₂ (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(OC₆H₃Prⁱ₂-

2,6)₃Cl₂]/3BuⁿLi 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 $[NbOC_6HPh_4-2,3,5,6)_3Cl_2]/3Bu^nLi$ containing 2,3,5,6-tetraphenylphenoxide ancillary ligation generates a reaction profile for PPh₃ in which the intermediate PPhCy₂ builds up dramatically (Fig. 3). This system can be used to synthetically prepare and purify PPhCy₂ 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 PPhCy₂ obtained by reacting P(C₆H₅)₃ with D₂ and P(C₆D₅)₃ with H₂ 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 [²H₁₂] and [²H₁₅] respectively, *i.e.* negligible H/D [²H] scrambling occurs during hydrogenation.

The hydrogenation of MePPh₂ by [Nb(OC₆HPh₄-2,3,5,6)₃Cl₂]/3BuⁿLi proceeds *via* intermediate MePPhCy with



Fig. 1 Reaction profile (fraction of products vs. the fraction hydrogenation) for the hydrogenation of PPh₃ by the mixture [Nb(OC₆H₃Pri₂-2,6)₂Cl₃]/4BuⁿLi (OC₆H₃Pri₂-2,6) = 2,6-diisopropylphenoxide). The solid black lines represent the reaction profile predicted by the kinetic model shown.

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Fig. 2 Reaction profile (fraction of products vs. the fraction hydrogenation) for the hydrogenation of dppm by the mixture [Nb(OC₆H₃Pri₂-2,6)₃Cl₂]/3BuⁿLi (OC₆H₃Pri₂-2,6) = 2,6-diisopropylphenoxide). The solid coloured lines do not represent a kinetic model but simply show the trends.



Fraction hydrogenation Fig. 3 Reaction profile (fraction of products *vs.* the fraction hydrogenation) for the hydrogenation of PPh₃ by the mixture [Nb(OC₆HPh₄-2,3,5,6)₃Cl₂]/3BuⁿLi (OC₆HPh₄-2,3,5,6 = 2,3,5,6-tetraphenylphenoxide). The solid black lines represent the reaction profile predicted by the kinetic model shown.



Fig. 4 ¹H NMR spectra of the aliphatic region (500 MHz, C₆D₆, 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(OC₆HPh₄-2,3,5,6)₃Cl₂]/3BuⁿLi (OC₆HPh₄-2,3,5,6 = 2,3,5,6-tetraphenylphenoxide) to carry out the reactions [P(C₆H₅)₃/H₂], [P(C₆H₅)₃/D₂] and [P(C₆D₅)₃/H₂]

a reaction profile modelled by a 2:1 ratio of rate constants, *i.e.* MePPh₂ is hydrogenated twice as fast as MePPhCy. The bulkier PriPPh₂, however, generates the chiral (unresolved) intermediate PriPPhCy in > 80% isolable yield (rate constant ratio of *ca*. 28:1). ¹H NMR of the PriPPh(C₆H₅D₆) obtained by reacting PriPPh₂ with D₂ again shows a predominantly all *cis* arene hydrogenation has occurred (Fig. 5).

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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(OC₆H₃Pri₂-2,6)₂Cl₃] (0.26 g, 0.47 mmol) and PPh₃ (2.5 g, 9.5 mmol) in benzene (17 ml). After the addition of BuⁿLi in hexane (3.0 ml of 0.5 mol l⁻¹, 1.5 mmol), the reactor was pressurized with H₂ (1200 psi initial pressure) and heated at 60 °C for varying amounts of time.

 \pm Selected data: ³¹P NMR (C₆D₆, 30 °C): for P(C₆H₅)₃, δ -4.93; P(C₆D₅)₃, -5.60; P(C₆H₅)₂(C₆H₁₁), -3.55; P(C₆H₅)₂(C₆H₅D₆), -3.85;



Fig. 5 ¹H NMR spectra of the aliphatic region (500 MHz, C_6D_6 , 30 °C) for P(Prⁱ)(C_6H_5)(C_6H_{11}) and P(Prⁱ)(C_6H_5)($C_6H_5D_6$) obtained using the mixture [Nb(OC₆HPh₄-2,3,5,6)₃Cl₂]/3BuⁿLi (OC₆HPh₄-2,3,5,6 = 2,3,5,6-tetraphenylphenoxide) to carry out the reactions [P(Prⁱ)(C_6H_5)₂/H₂] and [P(Prⁱ)(C_6H_5)₂/D₂]

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