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A new generation of homogeneous arene hydrogenation catalysts†

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The homogeneous hydrogenation of a variety of arene substrates can be catalysed by hydride derivatives of niobium and tantalum. A key feature of these catalysts is the presence of bulky ancillary aryloxide ligation. The systems demonstrate high regio- and stereo-selectivity in the hydrogenation of benzenes and polynuclear aromatic hydrocarbons. A unique characteristic of the niobium compounds is an ability to rapidly hydrogenate arylphosphine ligands, providing a new procedure for the synthesis of cyclohexylphosphine ligands.

Introduction

The field of arene hydrogenation chemistry will soon be entering its second century. The initial work of Sabatier on the interaction of finely divided nickel with ethylene was stimulated by Mond's earlier discovery of $[Ni(CO)_4]$.[1] Instead of isolating an ethylene derivative of nickel, serendipity led Sabatier to uncover the high activity of finely divided nickel for carrying out the hydrogenation of a variety of unsaturated organic substrates.[2] In 1901 with co-worker Senderens he 'attacked a case of hydrogenation, which up to that time had not been realized by any method, that of benzene'.[1] Not only did the experiment succeed, but the product obtained by the complete hydrogenation of benzene was, in fact, much purer (mp of 6 °C) than the sample of cyclohexane previously isolated by Markovnikov from Caucasian petroleum that had a mp of −11 °C![1,3] In subsequent papers Sabatier applied the method to a variety of mononuclear and polynuclear aromatic hydrocarbons with great success.[3] The discovery and development of this 'Sabatier method' led to the Nobel Prize (shared with Grignard) in 1912.

Following Sabatier's work, a variety of heterogeneous catalysts for arene hydrogenation was developed. Historically significant was the work of Adams on finely divided 'platinum-oxide, platinum black' (Adam's catalyst)[4] and the process of selectively digesting alloys to generate finely divided samples of metals (*e.g.* Raney nickel) by the industrial chemist Murray Raney.[5] The conversion of benzene to cyclohexane still represents the most important industrial hydrogenation reaction and is today carried out chiefly using a combination of Raney nickel and Ni/Al_2O_3 catalysts.[6] The product cyclohexane is primarily utilized in the production of adipic acid.

A more efficient utilization of sometimes expensive metals involves depositing the metal or its compounds onto suitable supports. Recently a number of materials obtained by attaching organometallic compounds to oxide surfaces have been shown to be highly active arene hydrogenation catalysts.[7]

The development of homogeneous catalysts capable of hydrogenating arene substrates has lagged well behind the heterogeneous systems. Following the original discovery of the so-called Wilkinson's catalyst[8] the field of homogeneous transition-metal catalysed alkene hydrogenation has grown into a large and sophisticated area of chemistry.[9] Despite this there is a relative dearth of systems that will hydrogenate benzene rings.[10,11] The majority of these systems are based upon middle and later transition metals and in some situations successful reactivity is limited to polynuclear aromatic hydrocarbon substrates. In certain cases, valuable mechanistic studies have been carried out,[10,12] although not all of these systems have been proven to be homogeneous. One system of particular note is an allyl–cobalt catalyst developed by Muetterties *et al.*[10] where NMR experiments led to the conclusion that the $C_6D_6H_6$ obtained by treating C_6D_6 with H_2 was an all-*cis* isotopomer.[13] This result has recently been confirmed using ion–molecule chemistry.[14] The hydrogenation of aromatics by Ziegler type catalysts utilizing nickel or cobalt alkoxides, acetylacetoates or carboxylates and trialkylaluminium activators has been known for some time.[15] The most significant of these is the 'Dimersol' process developed by the Institut Francais du Petrole (IFP), a homogeneous system that appears to be a viable alternative to heterogeneous technology for the large scale hydrogenation of benzene.[15]

During our studies of the early d-block metal chemistry that can be supported by sterically bulky aryloxide ligation[16] we discovered that mixed hydrido aryloxide derivatives of niobium and tantalum would carry out the intra- and inter-molecular hydrogenation of arene rings. This Feature Article highlights both the synthetic utility of the new catalysts as well as our present mechanistic knowledge.

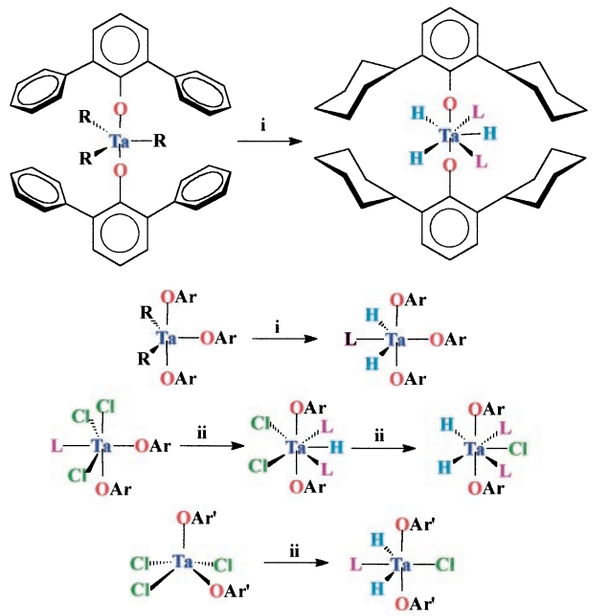
Synthesis and characterization of niobium and tantalum hydrido aryloxides

Of the many strategies available for the synthesis of transition-metal hydrides, two procedures are successful at generating mixed hydrido aryloxide derivatives of niobium and in particular tantalum (Scheme 1).[17] The first involves the high-pressure hydrogenolysis[18] of hydrocarbon solutions of mixed alkyl/aryloxides, typically in the presence of phosphine donor ligation. In some instances the hydrogenolysis is slow even under forcing conditions and only the alkyl precursor is reclaimed. In the case of aryloxide ligation containing *ortho*-phenyl substituents, the products isolated contain 2,6-dicyclohexylphenoxide groups (Scheme 1).[19] Under no circumstances have we detected the hydrogenation of phenyl rings either *meta* or *para* to the aryloxide oxygen or of the phenoxide nucleus itself. This is a highly significant result as it shows that these reaction mixtures do not contain small amounts of indiscriminate, possibly heterogeneous, arene hydrogenation catalysts. This selectivity coupled with an analysis of the stereochemistry of the reaction utilizing D_2 reagent gas and isolation of intermediates (*vide infra*) shows that the hydrogenation occurs in an intramolecular fashion within the niobium or tantalum compound itself.[19]

The second route to hydride derivatives involves treatment of the corresponding chloro aryloxides with Bu^n_3SnH in the presence of a donor phosphine (Scheme 1).[17] In the case of niobium, evolution of H_2 and formation of hydrogenation inactive d^1 species such as all-*trans*-$[Nb(OC_6H_3Pr^i_2\text{-}2,6)_2Cl_2(L)_2]$ (L = tertiary phosphine) takes place,[20] whereas discrete d^0 hydride compounds can be isolated for tantalum. The reaction does not lead to total substitution of all Ta–Cl bonds, but the procedure can be readily scaled up as well as modified by the use of commercially available Bu^n_3SnD to produce the corresponding deuteriated derivatives.[17]

The d^0 hydrides so far isolated fall into two broad categories. With two moderately bulky aryloxides, seven coordinate bis(phosphine) derivatives are isolated. These compounds contain a pentagonal-bipyramidal structure with mutually *trans*-axial phenoxide oxygen atoms (Scheme 1). The characteristically low field chemical shift of the Ta–H resonances not only aids in characterization, but careful analysis of the hydride signals shows these molecules to be stereochemically rigid on the NMR timescale.[17]

With the bulkier 2,6-di-*tert*-butylphenoxide or with three 2,6-diisopropylphenoxide ligands, six-coordinate mono(phosphine) species are generated (Scheme 1). The two structurally characterized examples show a distinct distortion away from octahedral geometry (*e.g.* Fig. 1).[17] In both cases the mutually *trans* hydride ligands are bent towards the Ta–P bond. These X-ray diffraction results are supported by IR studies which confirm the acute H–Ta–H angles (intensities of the symmetric and asymmetric stretching vibrations).[17] The origins of these distortions are beyond the scope of this review, but theoretical analysis points to σ bonding effects (not π bonding) as being important.[21]



Scheme 1 OAr = 2,6-diisopropyl, OAr′ = 2,6-di-*tert*-butylphenoxide, L = tertiary phosphine, R = $CH_2C_6H_4Me$-4. *Reagents and conditions*: i, H_2 (1200 psi), 80 °C; ii, Bu^n_3SnH, L.

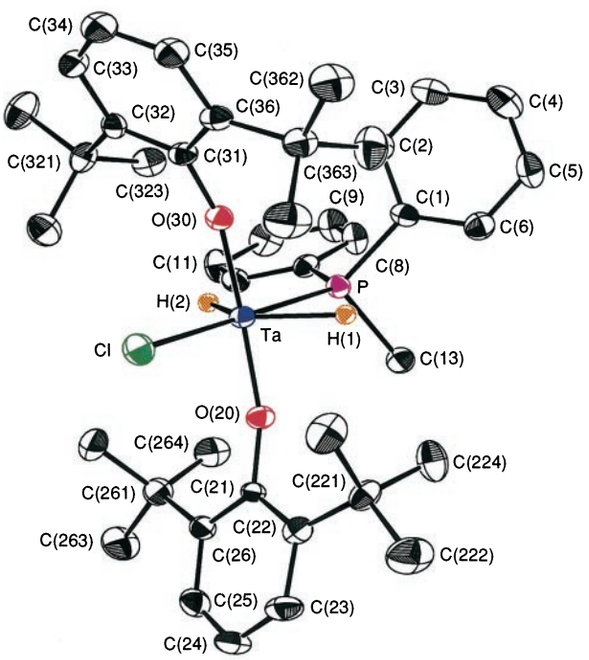


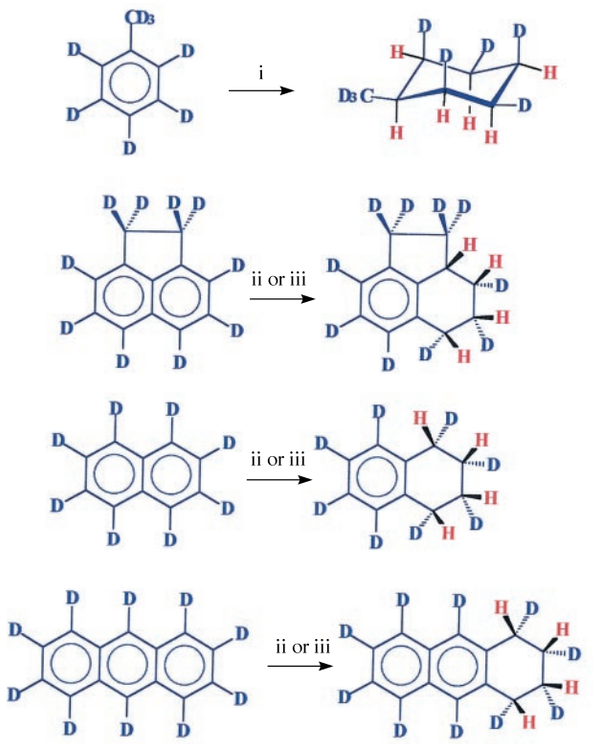
Fig. 1 ORTEP view of $[Ta(OC_6H_3Bu^t_2\text{-}2,6)_2Cl(H)_2(PMePh_2)]$

Intermolecular hydrogenation of arene rings: regio- and stereo-selectivities

Hydrocarbon solutions of the isolated tantalum trihydrides $[Ta\{OC_6H_3(C_6H_{11})_2\text{-}2,6\}_2(H)_3(PMe_2Ph)_2]$ and $[Ta(OC_6H_3\text{-}Pr^i_2\text{-}2,6)\}_2(H)_3(PMe_2Ph)_2]$ will catalyse the hydrogenation of naphthalene and anthracene at 80 °C under a hydrogen pressure of 50–1500 psi (psi ≈ 6.895×10^3 Pa).[24] When the hydrogenation of naphthalene is carried out in C_6D_6 solvent in a high-pressure 5 mm ^1H NMR tube, complete conversion of 20 equiv. of naphthalene to tetralin occurs with no decrease in the intensity of the tantalum hydride signals in the ^1H NMR spectrum. Only trace amounts of cyclohexane are formed in this reaction, indicating a much slower attack on the benzene solvent. In the cases of anthracene, almost exclusive formation of 1,2,3,4-tetrahydroanthracene precedes formation of 1,2,3,4,5,6,7,8-octahydroanthracene with no detectable quantities of 9,10-dihydroanthracene (typical of radical catalysts[22] and Birch type reductions[23]) being formed.

These hydride catalysts exhibit strong inhibition by added phosphine and this sensitivity to even trace amounts of free phosphine hinders kinetic analysis of the reactivity. This observation is consistent with an initial dissociation of at least one Ta–PR_3 bond in the seven-coordinate hydrides prior to substrate hydrogenation.

The hydrogenation of $[^2H_8]$naphthalene, $[^2H_{10}]$anthracene and $[^2H_{10}]$acenaphthene by hydride $[Ta\{OC_6H_3(C_6H_{11})_2\text{-}2,6\}_2(H)_3(PMe_2Ph)_2]$ produced single isotopomers as shown (Scheme 2).[24] Analysis of the ^1H and ^{13}C NMR spectra confirmed a highly selective, all-*cis* hydrogenation had oc-



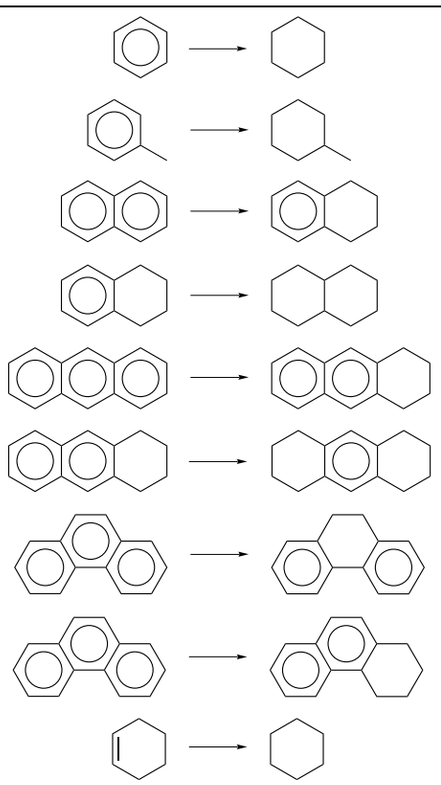
Scheme 2 *Reagent and conditions*: i, $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]/3Bu^nLi$, 80 °C, 1200 psi H_2, ii, $[Ta(OC_6H_3Pr^i\text{-}2,6)_3(H)_3(PMePh_2)_2]$, 80 °C, 1200 psi H_2; iii, $[Nb(OC_6H_3Ph_2\text{-}2,6)_2(CH_2C_6H_4Me\text{-}4)_3]$, 80 °C, 1200 psi H_2

curred with no H/D scrambling within either unreacted substrate or products. The all-*cis* nature of [$^2H_8$]tetralin has also been confirmed by ion–molecule techniques.[25]

The hydrogenolysis of alkyls of stoichiometry $[M(OAr)_2R_3]$ and $[M(OAr)_3R_2]$ (M = Nb, Ta) would be expected to generate base-free tri- and di-hydrides respectively. Although hydrides of this stoichiometry have not been isolated, the solutions thus generated are more active arene hydrogenation catalysts than the phosphine adducts, with niobium showing higher activity than tantalum and a stereoselectivity identical to that found for isolated tantalum catalysts such as $[Ta\{OC_6H_3(C_6H_{11})_2\text{-}2,6\}_2(H)_3(PMe_2Ph)_2]$ (Scheme 2).

An alternative, more synthetically straightforward procedure for carrying out the hydrogenation of arene substrates involves mixing the chloride precursors $[Nb(OAr)_3Cl_2]$ and $[Nb(OAr)_2Cl_3]$ (ArO = 2,6-diisopropyl-, 2,6-diphenyl- or 2,3,5,6-tetraphenyl-phenoxide) with 2–3 equiv. of Bu^{n}Li followed by exposure to H_2.[26] This procedure allows the hydrogenation to be carried out under milder conditions where hydrogenolysis of Nb–CH_2SiMe_3 and Nb–CH_2Ph bonds is slow. The niobium catalysts obtained by these methods demonstrate almost identical regio- and stereo-selectivity compared to the tantalum hydride systems.[24] Individual experiments as well as competition reactions show the relative rates of attack on arene substrates shown (Table 1).

Table 1 Relative rates of hydrogenation of aromatic hydrocarbons compared to benzene at 100 °C



	1[a]
	0.4[b]
	7[c]
	0.35[c]
	21[c]
	3[c]
	1.3[c]
	0.7[c]
	25 (25 °C)[d]

[a] $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]$/3Bu^{n}Li, 100 °C, 0.464 mmol Nb, 190 mmol C_6H_6 (409 per Nb), volume 20 ml, 1 h, 1200 psi H_2, analysed by GC. [b] $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]$/3Bu^{n}Li, 100 °C, 0.464 mmol Nb, 95 mmol C_6H_6 (200 per Nb), 95 mmol C_6H_5Me (200 per Nb), volume 20 ml, 1 h, 1200 psi H_2, analysed by GC. [c] $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]$/3Bu^{n}Li, 100 °C, 0.464 mmol Nb, 190 mmol C_6H_6 (409 per Nb), 9.5 mmol substrate (20 per Nb), volume 20 ml, 1–6 h, 1200 psi H_2, analysed by GC and corrected for concentration of substrate. [d] $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]$/3Bu^{n}Li, 25 °C, 0.464 mmol Nb, 95 mmol C_6H_6 (200 per Nb), 95 mmol Nb, 95 mmol C_6H_8 (200 per Nb), volume 20 ml, 1–6 h, 1200 psi H_2, analysed by GC.

These results indicate that selectivity is determined by the coordination affinity of the arene ring and steric factors. Anthracene is hydrogenated faster than naphthalene to initially produce 1,2,3,4-tetrahydroanthracene. Attack on this (essentially a 2,3-disubstituted naphthalene) yields exclusively octahydroanthracene. Consistent with this is the preference for attack on the unsubstituted ring of 2-methylnaphthalene.[24] The hydrogenation of naphthalene by the alkyl precursors $[Nb(OC_6H_3Ph_2\text{-}2,6)_2(CH_2C_6H_4Me\text{-}4)_3]$ in cyclohexane only occurs at temperatures above 50 °C but reaches a plateau of maximum activity above 100 °C (Fig. 2).

Further hydrogenation of tetralin produces predominantly *cis*-decalin (*cis*/*trans* = 9) but at a rate an order of magnitude slower than the formation of tetralin. The hydrogenation of benzene by the $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]$/3Bu^{n}Li system is slower than initial attack on naphthalene. A drop in activity is again observed at too high a temperature, possibly indicative of thermal instability of the catalyst. Toluene undergoes hydrogenation 2.5 times slower than benzene and the methylcyclohexane produced by hydrogenation of [$^2H_8$]toluene has been shown by NMR methods to be the all-*cis* isotopomer (Scheme 2).

These catalysts also show high activity for the hydrogenation of alkenes and dienes. The hydrogenation of cyclohexene occurs much faster and under much milder conditions than the corresponding hydrogenation of aromatic substrates (Table 1).

All of these catalysts/precursors suffer from a sensitivity to protic impurities and dioxygen. In order for catalytic activity to be achieved and maintained the substrates, solvents and equipment must be thoroughly dried and the reaction set up with precautions being taken to prevent contamination by air or moisture. This normally requires the pressure reactors being charged and assembled within a Dri-Lab facility.

Mechanistic considerations

A preference to undergo substitution reactions rather than addition chemistry is a defining characteristic of aromatic compounds. Consideration of the heats of formation (kcal mol^{-1}, cal = 4.184 J) of gaseous benzene (19.8), cyclohexa-1,3-diene (25.6), cyclohexene (−0.9) and cyclohexane (−29.4)[27] show that the generation of cyclohexa-1,3-diene is the problematic (endothermic) step in the hydrogenation of benzene. Furthermore, on purely thermodynamic arguments it appears a daunting task to design a combination of catalyst and conditions which will lead to only the partial hydrogenation of benzene. The success of Birch reductions[23] and related reactions at stoichiometrically generating partially hydrogenated products (typically 1,4-dienes) is due to the much higher electron affinity of the arene substrate over the products. The conversion of benzene to cyclohexene is thermodynamically favourable, and the monoene is a highly desired product. Recently there has been some success in the development of heterogeneous catalysts for converting benzene into cyclohexene.[28] Thermodynamic analysis of the stoichiometric reaction of a transition-metal dihydride with ethylene followed by oxidative addition of H_2 shows that both steps can be exothermic leading to a viable catalytic cycle. In contrast although the corresponding reaction with benzene to produce cyclohexa-1,3-diene may conceivably be exothermic, such a dihydride must be thermodynamically unstable with respect to loss of H_2. The partial saturation of fused-ring aromatic compounds does not suffer from as dramatic a loss of resonance stabilization, *e.g.* conversion of naphthalene to 1,2-dihydronaphthalene is exothermic. This accounts for the more facile hydrogenation of polynuclear aromatic hydrocarbons by heterogeneous and homogeneous systems compared to single ring aromatics. This hypothesis is given strong support in the reaction chemistry of main-group hydride reagents. In particular the mammoth body of work dealing with the stoichiometric hydroboration of alkenes[29] contrasts with the Lilliputian studies

involving arene substrates.[30] A large number of transition-metal hydride compounds are stable in aromatic solvents. When reactivity does occur, it commonly involves aromatic C–H bond activation either *via* oxidative-addition pathways (sometimes preceded by H_2 elimination)[31] or else by σ-bond metathesis with highly electrophilic d^0 metal hydrides.[32]

Our attempts to understand these Group 5 metal-catalysed reactions has led us to volunteer the mechanistic pathways shown in Scheme 3. We have attempted with some success to isolate and study some of the reasonable intermediates in this catalytic cycle. Considerable experimental evidence has been obtained that the niobium and tantalum aryloxides can strongly bind to cyclohexa-1,3-diene intermediates produced by transfer of two hydrogen atoms to an arene ring. An intramolecular example of this is the formation of a chelated cyclohexadiene species generated *via* attack on an *ortho*-phenyl phenoxide ligand by an intermediate niobium dihydride.[19] Although we have as yet not detected the stoichiometric, intermolecular attack of an isolated niobium or tantalum hydride on a benzene ring, a series of cyclohexa-1,3-diene derivatives can be readily obtained by reduction methods (Scheme 4).[33] The structural parameters for these species indicate a significant contribution

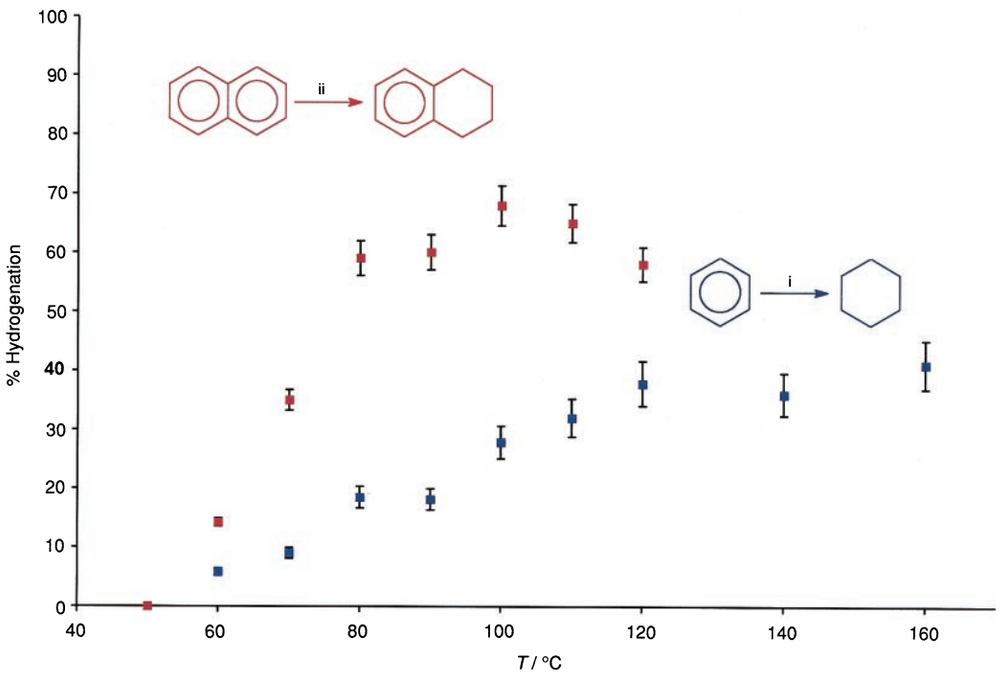
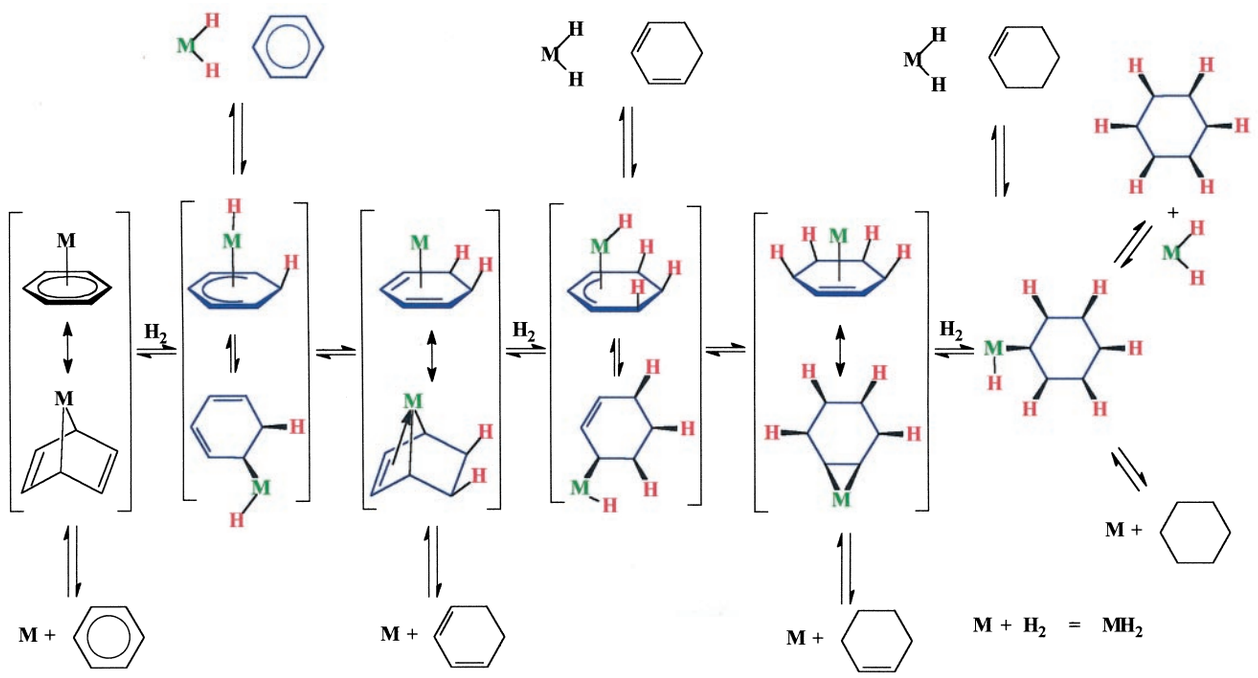


Fig. 2 Temperature dependence of the hydrogenation of benzene and naphthalene. *Reagents and conditions*: i, $[Nb(OC_6HPh_4-2,3,5,6)_2Cl_3]/3Bu^nLi$, 0.464 mmol Nb, 190 mmol C_6H_6 (409 per Nb), volume 20 ml, 6 h, 1200 psi H_2; ii, $[Nb(OC_6H_3Ph_2-2,6)_2(CH_2C_6H_4Me-4)_3]$, 0.1 mmol, 20 mmol $C_{10}H_8$ (200 per Nb), volume 3 ml, C_6H_{12} solvent, 6 h, 1200 psi H_2.

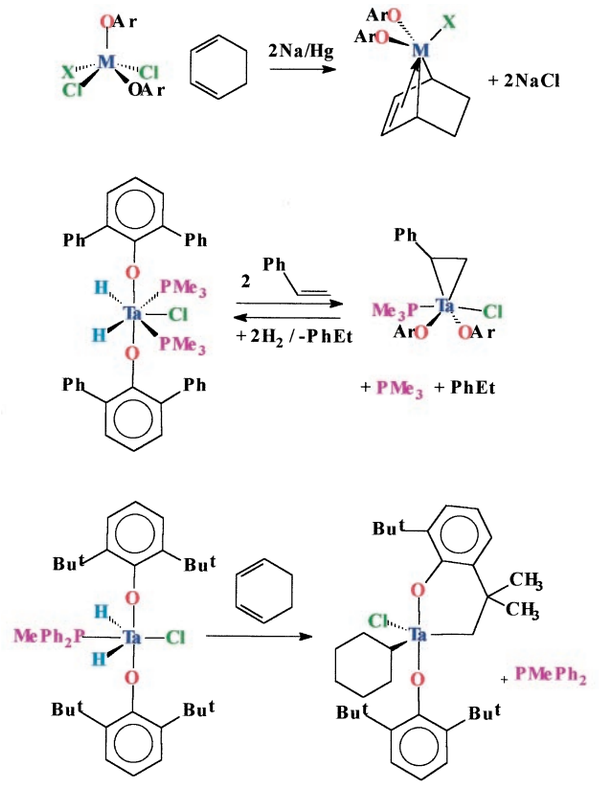


Scheme 3

from a metallanorbornene (d^0 metal) bonding picture.[34] Some important observations are the fact that dissociation or displacement of cyclohexa-1,3-diene from these compounds is difficult and that they react with H_2 under very mild conditions to liberate cyclohexane. Species of this type are, therefore, reasonable intermediates during the catalytic cycle, but are found to react rapidly with H_2 under the conditions at which arene hydrogenation is carried out.[33] The strong binding of the cyclohexa-1,3-diene fragment to niobium and tantalum metal centres also accounts for the preference for an all-*cis* hydrogenation in intermolecular arene hydrogenation. The niobium compound [Nb($OC_6H_3Pr^i_2$-2,6)$_3$(η^4-C_6H_8)] will catalyse the hydrogenation of cyclohexa-1,3-diene and cyclohexene under very mild conditions. Mechanistic studies show that cyclohexa-1,3-diene is hydrogenated selectively over cyclohexene. Furthermore labelling studies show that intermediate cyclohexene is not released during the hydrogenation of cyclohexa-1,3-diene.[33,35] In contrast the less active catalyst [Nb(OC_6H_3-Pr^i_2-2,6)$_2$Cl(η^4-C_6H_8)] converts cyclohexa-1,3-diene into cyclohexene prior to formation of cyclohexane. These results show how slight changes in the ligand environment of a homogeneous catalyst can lead to dramatically different selectivity.

The proposed mechanistic pathway (Scheme 3) proceeds next *via* a cyclohexene complex. Although no cyclohexene complex has yet been isolated, the stoichiometric reaction of the tantalum dihydride [Ta($OC_6H_3Ph_2$-2,6)$_2$Cl(H)$_2$(PMe_3)$_2$] with styrene has been shown to produce 1 equiv. of ethylbenzene and a styrene complex (Scheme 4).[36]

The solid-state structure of this product shows the presence of a tantacyclopropane ring and in solution dissociation or exchange of bound styrene is slow, again showing how formally d^2 fragments such as [M(OAr)$_3$] or [M(OAr)$_2$Cl] will strongly bind to unsaturated groups.[36] Treatment of the styrene complex with H_2 regenerates the initial dihydride along with another equivalent of ethylbenzene (Scheme 4). The final, partially hydrogenated intermediate in the catalytic cycle is a cyclohexyl–metal species (Scheme 3). The stoichiometric reaction of



Scheme 4 M = Nb, Ta; OAr = 2,6-diisopropylphenoxide; X = Cl, OAr

cyclohexa-1,3-diene with dihydride [Ta($OC_6H_3Bu^t_2$-2,6)-Cl(H)$_2$($PMePh_2$)] produces a stable cyclohexyl compound (Scheme 4); the third equivalent of hydrogen originating by C–H bond activation (cyclometallation) of one of the 2,6-di-*tert*-butyl phenoxide ligands.[37]

Clearly much more mechanistic work is needed on these and other model systems to gain a better understanding of the arene hydrogenation chemistry. In particular mention should be made of an alternative mechanistic pathway involving initial activation of the arene by coordination to a d^2 metal fragment. This reaction certainly has precedence in Group 5 metal chemistry, particularly in the work of the Wolczanski[38] and Wigley[34,39] groups. The extremely reactive d^2 [Ta(silox)$_3$] species will coordinate and activate a multitude of unsaturated substrates including benzene and heterocyclic compounds.[38] During studies of alkyne oligomerization, Wigley and co-workers have shown that strong bonding of arenes takes place to d^2 [Ta(OAr)$_2$Cl] fragments and a tantalanorbornadiene bonding picture has been proposed.[34] The hydrogenolysis of one of the metal–carbon bonds in this species would generate the same cyclohexadienyl hydride as formed by insertion of a d^0 metal–hydride bond across benzene (Scheme 3). During our studies of the chemistry of low-valent aryloxides of tungsten we have isolated a series of 16-electron compounds in which η^6-binding of an *ortho*-phenyl ring of a 2,3,5,6-tetraphenylphenoxide ligand occurs.[40] These compounds react with certain ketones to produce products that can be considered as originating from a tungstanorbornadiene ground-state structure.[41] Reaction with H_2 takes place under very mild conditions to produce an *ortho*-cyclohexene ring.[40] Our present knowledge of species such as [Nb($OC_6H_3Pr^i_2$-2,6)$_3$] and [Ta($OC_6H_3Pr^i_2$-2,6)$_2$Cl] is that they undergo rapid intramolecular dehydrogenation of *ortho* Pr^i groups even in the presence of benzene.[36,42] Clearly further studies are needed to determine conclusively whether one or both of these pathways are operating in these catalytic systems.

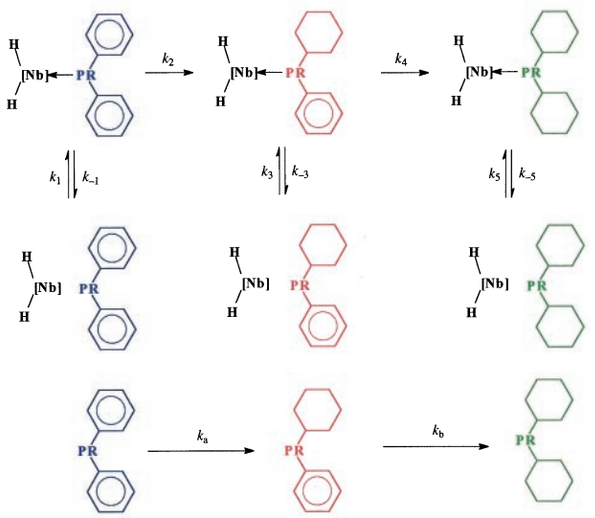
Catalytic hydrogenation of arylphosphines: a novel case of heteroatom insensitivity

When the tantalum dihydride [Ta($OC_6H_3Pr^i_2$-2,6)$_3$-(H)$_2$($PMePh_2$)] is heated under hydrogen pressures for days, the stepwise formation of the cyclohexylphosphine species [Ta($OC_6H_3Pr^i_2$-2,6)$_3$(H)$_2${PMe(C_6H_{11}Ph)}] and [Ta(OC_6H_3-Pr^i_2-2,6)$_3$(H)$_2${PMe(C_6H_{11})$_2$}] is observed by ^{1}H and ^{31}P NMR spectroscopy.[17] In the field of transition-metal mono-, di- and poly-hydride chemistry the phosphine ligand is a dominant ancillary.[43] Furthermore, by far the vast majority of alkene hydrogenation catalysts contain phosphine ligation as a critical component, particularly systems where a chiral phosphine auxiliary causes asymmetric hydrogenation of a prochiral substrate. In none of these situations has the hydrogenation of aryl groups attached to phosphorus been documented. Any vexing interference by arylphosphines typically involves cyclometallation of arene CH bonds,[44] π-complexation with the metal[45] or hydrogenolysis of P–C bonds leading to inert metal phosphide species.[46] The niobium arene hydrogenation systems exhibit much greater activity than the tantalum hydrides for the hydrogenation of arylphosphines. This reactivity has been utilized to develop a new synthetic procedure for the formation of cyclohexylphosphines from their cheaper, readily available phenylphosphine counterparts.[47] The success of the niobium compounds for carrying out the reaction is remarkable and must rely on a number of important features. The coordination of the substrate phosphine ligand acts as a 'Trojan Horse' bringing in close proximity to the metal the aryl group. However, carrying out the total saturation of the phenyl ring undoubtedly necessitates breaking at various stages the Nb–P bond. The success of the reaction not only depends on facile exchange of substrate/product phosphine groups within the metal coordination sphere, but also on the fact that the much greater basicity

of cyclohexylphosphines must be offset by their larger cone angle.[48] A much stronger binding of one of the product phosphine ligands could effectively shut down the catalysis. We have also studies the course of these reactions by ^{31}P NMR analysis at intermediate stages of hydrogenation. In no cases have we been able to detect significant quantities of cyclohexadienyl- or cyclohexenyl-phosphine compounds. The build up and decay of intermediate cyclohexylphenylphosphines can be readily illustrated by a reaction profile in which the fraction of products is plotted against the fraction hydrogenation of the sample. Some interesting information can be gained from these plots. In the case of the hydrogenation of PPh_3 by the catalyst system $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]/3Bu^nLi$ the dramatic build up of the final intermediate $PPh(C_6H_{11})_2$ can be seen (Fig. 3).

This reaction profile can be simulated accurately using a simple kinetic model involving sequential first-order rate constants.[26] The success of this kinetic model for the reaction places constraints on the rate constants within a more complex model in which rates of phosphine coordination and dissociation are included. Although many regimes can exist for this model, the restraint that the rates of phosphine association/dissociation are faster than the rate of saturation of the arene ring means that the first-order constants from the simple model are proportional to the product of the formation constants of the metal phosphine and the rate of arene ring hydrogenation. This is highlighted in Scheme 5 for an alkyldiphenylphosphine. The low relative rate of hydrogenation of $PPh(C_6H_{11})_2$ (Fig. 3) may, therefore, be ascribed either to a low formation constant for the bulky phosphine and/or relatively slow attack on the P–Ph group within this particular ligand. By exploiting this reaction profile we have been able to synthesize the deuteriated compounds $[P(C_6H_5)(C_6H_5D_6)_2]$ and $[P(C_6D_5)(C_6D_5H_6)_2]$ and show that the reaction occurs in a predominantly all-*cis* fashion for attack at both phenyl rings.[26] The detection of non-all-*cis* stereoisomers is almost certainly a consequence of the intermediate regiochemistry of the reaction.[19]

Due to the much documented lack of inversion of configuration at phosphorus under ambient conditions, substrates of stoichiometry $RPPh_2$ are prochiral. We find that the build up of the intermediate, chiral (unresolved) alkyl, phenyl, cyclohexylphosphine can be enhanced by increasing the bulk of the alkyl substituent (Table 2). In the case of $[Pr^iPPh(C_6H_5D_6)]$, labelling studies again show a predominance of all-*cis* hydrogenation.[26] The use of phosphines with chiral alkyl groups leads to diastereomeric pairs. Analysis by ^{31}P NMR indicates a slight diastereomeric excess for the alkyls so far examined (Fig. 4, Table 2), showing the successful transfer of chirality from a carbon atom to an adjacent phosphorus centre.[49]



Scheme 5 If k_1, k_{-1}, k_3, $k_{-3} \gg k_2$, k_4 then $k_a/k_b = (k_1/k_{-1})k_2/(k_3/k_{-3})k_4$

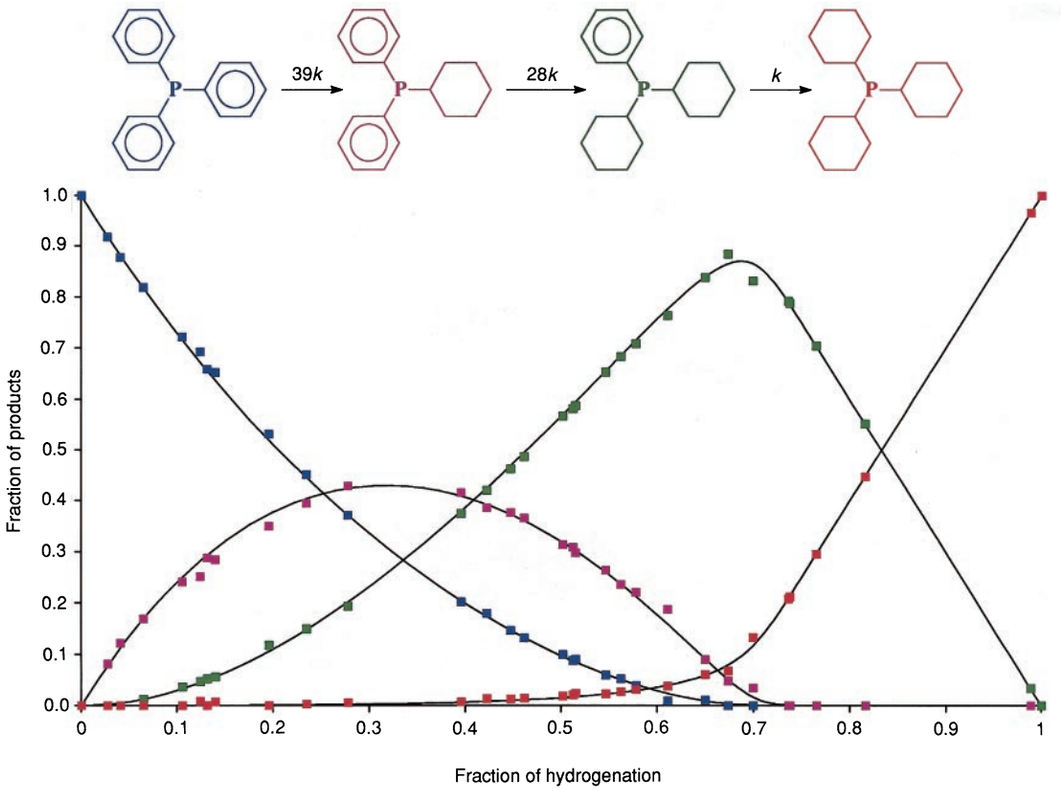


Fig. 3 Reaction profile for the hydrogenation of PPh_3 by $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]/3Bu^nLi$, 0.464 mmol Nb, 190 mmol C_6H_6 (409 per Nb), 9.5 mmol PPh_3 (20 per Nb), volume 20 ml, 60 °C, 1200 psi H_2

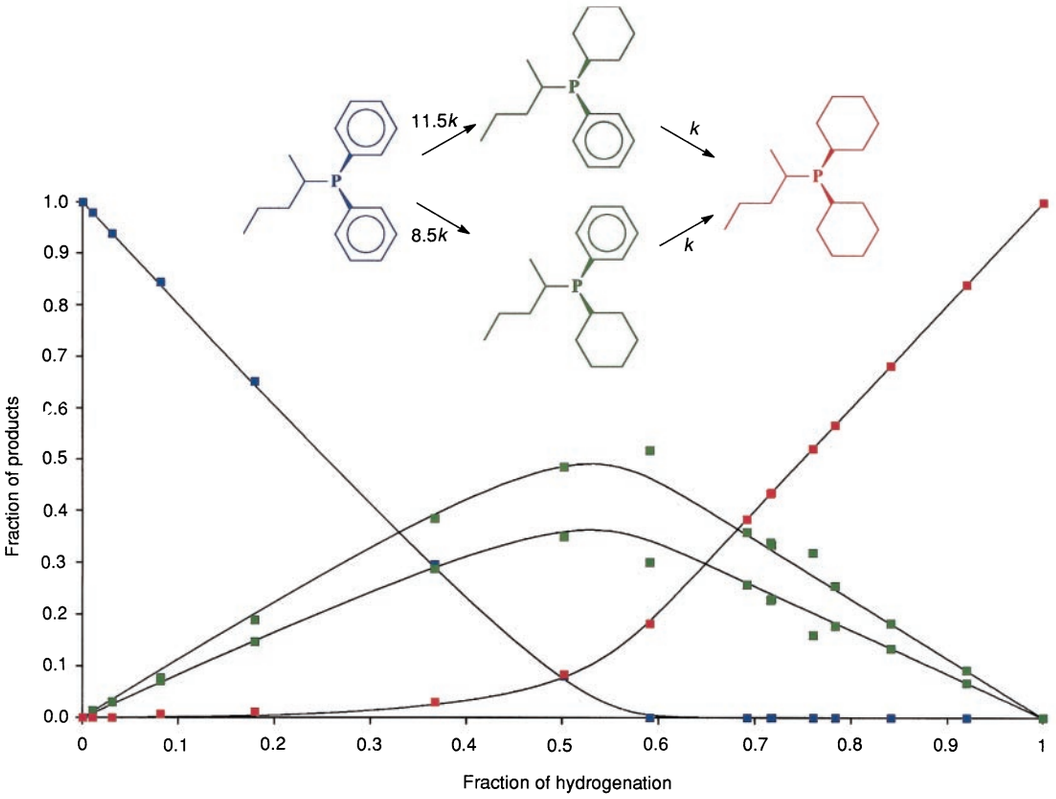
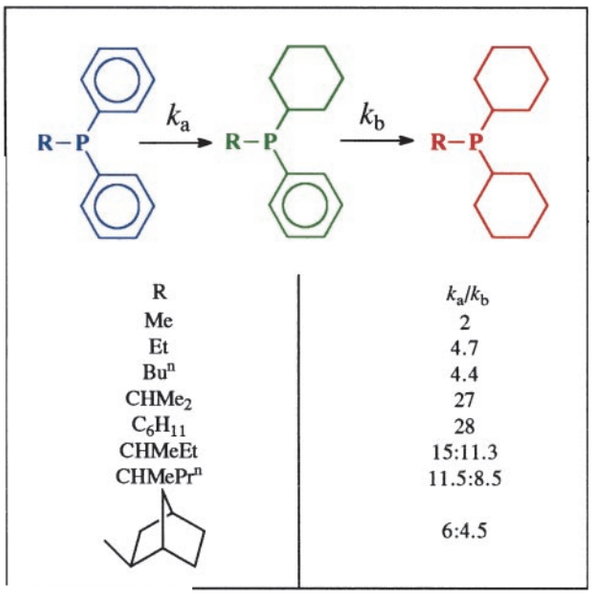


Fig. 4 Reaction profile for the hydrogenation of [(s-C_5H_{11})PPh_2] by [Nb(OC_6HPh_4-2,3,5,6)$_2Cl_3$]/3Bu^{n}Li, 0.464 mmol Nb, 190 mmol C_6H_6 (409 per Nb), 9.5 mmol [(s-C_5H_{11})PPh_2] (20 per Nb), volume 20 ml, 60 °C, 1200 psi H_2

Table 2 Ratio of rate constants for hydrogenation of alkyldiphenylphosphines[a]



R	k_a/k_b
Me	2
Et	4.7
Bu^n	4.4
$CHMe_2$	27
C_6H_{11}	28
CHMeEt	15:11.3
$CHMePr^n$	11.5:8.5
	6:4.5

[a] [Nb(OC_6HPh_4-2,3,5,6)$_2Cl_3$]/3Bu^{n}Li, 60 °C, 0.464 mmol Nb, 190 mmol C_6H_6 (409 per Nb), 9.5 mmol $RPPh_2$ (20 per Nb), volume 20 ml, 1200 psi H_2, analysed by ^{31}P NMR and k_a/k_b obtained by simulation.

The mild conditions used in these studies will not lead to racemization on the timescale of the experiment. It is clearly possible to envision adapting these systems for catalytically generating enantiomeric excesses of chiral phosphine ligands.

The hydrogenation of the bis(phosphine) substrates $Ph_2P(CH_2)_nPPh_2$ (n = 1–6) leads to the corresponding cyclohexyl derivatives. The reactions profile for the hydrogenation of dppm by [Nb($OC_6H_3Pr^i_2$-2,6)$_2Cl_3$]/3Bu^{n}Li shows the build up of product dcpm even at low fraction hydrogenation.[26] This indicates that in this case the rate of hydrogenation of the P–Ph group is faster than the rate of dissociation from the catalytically active site.

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Footnote

† This ChemComm is also available in enhanced multi-media format *via* the World Wide Web: http://chemistry.rsc.org/rsc.cccenha.htm

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