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# Catalytic applications of small bite-angle diphosphorus ligands with single-atom linkers

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Diphosphorus ligands connected by a single atom ($R_2PEPR_2$; E = $CR_2$, $C{=}CR_2$ and NR) give chelating ligands with very small bite angles (natural bite angle of 72° for dppm) as well as enable access to other properties such as bridging modes and hemilablity. Their use in catalysis has been growing over the last two decades as researchers have sought to apply the properties of small bite-angle ligands to a wide number of catalytic reactions, often complementing the well-established applications of wide bite-angle ligands in catalysis. This *Perspective* reviews the properties of diphosphorus ligands featuring a single-atom linker and their use in several catalytic transformations of alkenes, including selective ethene oligomerisation, ethene polymerisation and co-polymerisation with CO, hydroacylation and hydrogenation, as well as their use in transfer hydrogenation and hydrogen-borrowing reactions.

## Introduction

The rational choice and design of ligands is important in order to control the reactivity of transition metals and facilitate their application in many fields, including catalysis.[1] Altering the bite angle of a bidentate ligand has two effects[1, 2] (Figure 1):

1. Ligands with wider bite angles are more sterically bulky and will exert more steric repulsion on the other ligands at the metal centre.
2. Enforcing a ligand bite angle has an electronic, or orbital, effect in pushing the metal centre towards a preferred geometry. For example, tetrahedral Ni(0) would prefer a ligand with a bite angle close to 109.5° whereas square planar Ni(II) would prefer a ligand with a bite angle of 90°.

Changing the bite angle of chelating diphosphines is readily achieved by increasing the chain of atoms linking the two phosphine donors. 1,2-Bis(diphenylphosphino)ethane (dppe) forms very stable 5-membered chelates, and comparisons with smaller or larger chelates can readily be achieved by changing the hydrocarbon linker. However, upon reaching $C_4$ linkers (*e.g.* 1,4-bis(diphenylphosphino)butane, dppb), the ligand has considerable flexibility and a reduced propensity for chelation.[3] Bridging bimetallic structures can then be favoured leading to different reactivity pathways and mechanisms that are no longer related to the bite angle. To develop useful, larger bite angle ligands more rigid architectures are required such as DPEphos, Xantphos or BINAP (Figure 1) that contain aromatic rings in the linker.[1, 4] Bis(diphenylphosphino)methane (dppm), and other small bite angle ligands that form four-membered chelates, also have a greater propensity to form other molecular architectures, so the effect of bite angle needs to be considered with these other effects.

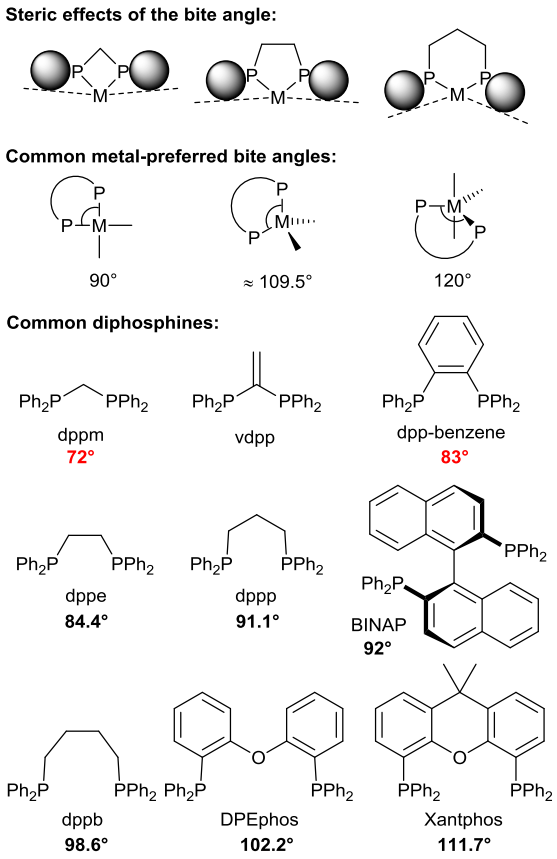


**Figure 1**. Steric effects and bite angles (natural bite angles, β, or X-ray derived values with standardised M-P distances and angles recalculated, shown in red) for diphosphorus ligands.[2]

Altering steric and electronic properties has a direct effect on metal reactivity and catalysis. It has been known for many years, and was usefully quantified for monodentate ligands by Tolman's cone angle approach,[5] that steric bulk has an

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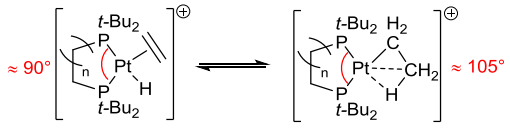
important role to play along with the σ-donor and π-accepting properties of a ligand. The cone angle for each P donor in a bidentate diphosphine can also be calculated as for the procedure for unsymmetrical phosphines with one half-angle taken to be the angle between the M-P bond and the P-M-P bisector.[6] More recent computational approaches[7, 8] to characterise diphosphine ligands include the $\%V_{bur}$ descriptor,[9] the implementation of steric maps to visualise the space constraints around a metal atom,[10] and the use of multiple descriptors such as applied in the Ligand Knowledge Base.[11, 12] Many subtle electronic factors have also emerged, and the effect of bite angle has become an important consideration in many catalytic reactions.[4, 13-15] It is important to note that while the effect of bite angle on one step of a reaction might be clear cut, catalytic cycles involve many reaction steps and equilibria, and the overall effect of bite angle can be harder to ascertain.[4] Also, the relative importance of the steric and orbital effects of changing the bite angle can differ with each particular system, and a number of theoretical studies have pointed to the steric effect being dominant.[16-18] However, several useful, general observations have been made:

1. **Changing the bite angle can effect equilibria between species in solution.** For example, in changing the equilibrium between a cationic Pt ethene hydride to an agostic Pt ethyl cation upon increasing the bite angle from a 5-membered chelate to a 6-membered chelate (Scheme 1).[19] This was predicted by theoretical considerations where a bite angle close to 110° (more recently revised to 100°)[20] would help stabilise the transition state for the migratory insertion reaction.[13, 21] The same trend was noted for Pd diphosphine complexes where $[Pd(dppe)(H)(alkene)]^+$ was found to be more stable than the corresponding dppp and dppb complexes.[4] The rate of CO insertion into M-R bonds follows the same trend of increasing rate with increasing bite angle for the reaction of several Pd and Pt complexes with CO.[2, 22-24] The geometry of $[Ru(diphosphine)_2(H)(H_2)]^+$ complexes are also influenced by bite angle effects.[25, 26]

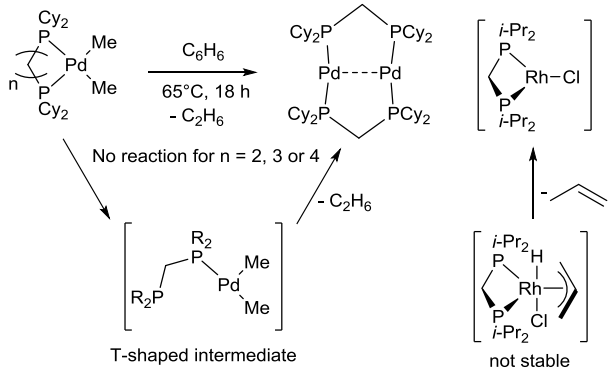



**Scheme 1**. Bite angle affecting an equilibrium.

2. **Influencing selectivities**. The ligand bite angle can affect the product selectivity in catalytic reactions, such as increased selectivity for the linear hydroformylation product when using larger bite angle ligands.[2, 4] This could be related to greater effective steric bulk at the metal centre leading to the less hindered linear alkyl complex, but the effect of equatorial-equatorial versus axial-equatorial coordination has also been discussed.[4] In a key computational study, the orbital effect arising from the bite angle (as opposed to the steric effect) was assessed to have little influence, with selectivity governed by the non-bonding effects that are also changed when the bite angle is changed.[18]

3. **Affecting rates of reductive elimination.** Reductive elimination reactions can be enhanced by two, somewhat complementary, mechanisms:[14] through three coordinate intermediates[27-29] or using wide bite angle bidentate ligands that favour zero valent metal centres over the 90° bond angles in square planar complexes.[13, 14] Early kinetic studies[30, 31] on the reductive elimination of R-R from *cis*-$[PdR_2(PMePh_2)_2]$ (R = Me, Et) found that the rate of the reaction was greatly reduced upon addition of small amounts of free $PMePh_2$, with the kinetic analysis suggesting that the reaction proceeds through a dissociative pathway involving a three coordinate intermediate that has lost one phosphine ligand.[30] One explanation of this observation is that direct reductive elimination from four-coordinate complexes would lead to non-linear $[M(PR_3)_2]$ intermediates of high energy.[32] Increasing the ligand bite angle has been found to increase the rate of reductive elimination in hydrocyanation catalysis[33] where wide bite angle ligands are required to destabilise square planar Ni(II) alkyl cyanide complexes and promote reductive elimination to form tetrahedral Ni(0).[4] However, it should be noted that dppe, dppp and dppb all gave yields of between 0 and 11%,[2] and that ligands with bite angles over 100° were required for effective catalysis indicating a minimum threshold for effective performance. Other mechanisms involving complexes with two $\kappa^1$-Xantphos ligands have also been discussed that do not imply an orbital bite angle effect.[34, 35]

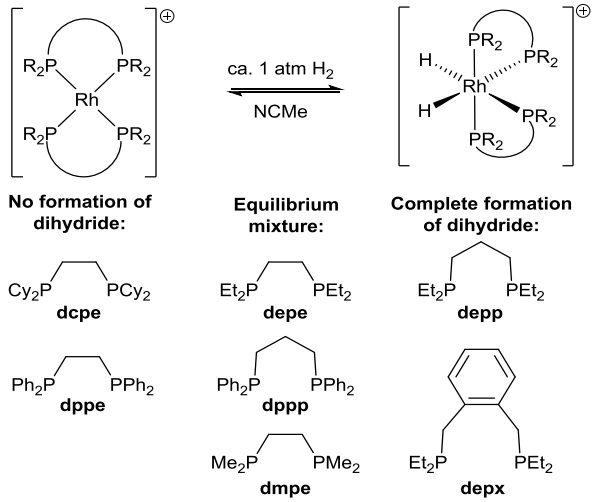
For $R_2PEPR_2$ ligands containing extremely small bite angles, reductive elimination can be favoured through the formation of three-coordinate intermediates driven by dissociation of one donor atom. Studies on the reductive elimination of ethane from $[Pd(Me)_2(diphosphine)]$ complexes have shown that only complexes with a single carbon atom between the two phosphine donors can undergo reductive elimination of ethane (Scheme 2).[32] Complexes with longer hydrocarbon linkers were not observed to react whereas changing the $R_2PCH_2PR_2$ substituents from Cy to $^t$Bu or Ph gave similar reactivity except that the intermediate $[Pd(diphosphine)Me_2]$ was not stable and rapidly eliminated ethane at room temperature.[32] Facile elimination of ethane from $[Ni(Me)_2(dppm)]$ has also been observed whereas complexes of the wider bite angle ligands dppe and dppp were stable.[36] Several articles invoke a "T-shaped intermediate" for the reductive elimination of ethane from $[Pd(diphosphine)R_2]$ complexes because retention of the chelating ligand would lead to a non-linear Pd(0) product of very high energy.[32, 37] $[Rh(C_3H_5)(H)(Cl)\{P(^iPr)_2CH_2P(^iPr)_2\}]$, a Rh(III) intermediate, could not be isolated due to fast reductive elimination (Scheme 2), whereas analogous $Rh(P^iPr_3)_2$ complexes are known.[38]




**Scheme 2**. Reductive elimination pathways for $R_2PCH_2PR_2$ complexes.

4. **Oxidative addition.** The effect of bite angle on the rate of oxidative addition reactions appears to be less clear-cut. Wide bite angle ligands have been used in cross coupling reactions in regimes where oxidative addition is not the rate limiting step because it is acknowledged that "wide bite angles do not accelerate oxidative addition".[14] Wide bite angle ligands are therefore not used for aryl chloride substrates, where bulky electron-rich phosphines are preferred instead, because oxidative addition is more challenging for these substrates.[39, 40] For the oxidative addition of Ar-Cl to $[Pd\{P(^iPr)_2(CH_2)_nP(^iPr)_2\}_2]$ complexes, numerous factors were shown to be important, including the electron-donating nature of the P substituents. Partial ligand dissociation can also occur leading to the formation of *trans* (both oligomers and the complex with two diphosphine ligands) as well as *cis* products.[3] Importantly, the complex where n = 2 was found to be of low reactivity due to the high stability of the bis(chelate) complex, whereas ligands with n = 3 and 4 gave similar rates, although different selectivities because with n =4, exclusively a *trans* product was observed.[3] Computationally, the mono-ligated species $[Pt(\kappa^2\text{-}PH_2CH_2PH_2)]$ was found to have lower barriers to the oxidative addition of H-$CH_3$ than $[Pt(\kappa^2\text{-}PH_2C_2H_4PH_2]$, which in turn had lower barriers than two monodentate $PH_3$ ligands.[41] The reasons behind this pattern of reactivity has been ascribed mainly to steric factors because chelating phosphines preform metal complexes with the P substituents bent away from the incoming substrate.[16, 17] Thus, the strain in pushing the ligands closer together upon oxidatively adding a C-X bond is reduced with smaller bite angles (not an orbital effect).[42, 43]

Several cases where oxidative addition has been favoured for larger bite angle ligands have been observed. This includes the observation that the oxidative addition of $H_2$ to $[Rh(diphosphine)_2]^+$ complexes forming *cis*-octahedral products was favoured for larger bite angle diphosphines, as well as small cone angles and electron donating substituents, but bite angle was the dominant effect (Scheme 3).[44, 45] However, very small chelates were not investigated. A mechanistic study of a hydroacylation reaction identified the small bite angle of bis(dicyclohexylphosphino)methane (dcpm) to be an important factor favouring oxidative addition of the aldehyde C-H bond, which was the rate limiting step.[46]



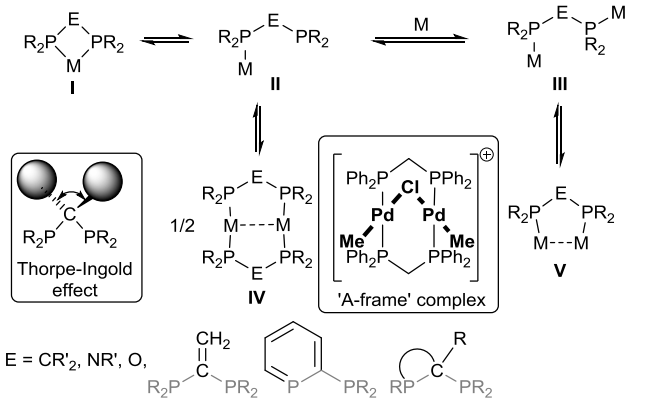

**Scheme 3**. The influence of diphosphine ligands on the oxidative addition of $H_2$ to Rh(I).

Overall, there is mixed evidence that very small bite angle ligands could be advantageous for oxidative addition reactions because many other factors need to be taken into consideration such as the nature of the different species in solution and the geometries of the species involved. Stable complexes with unstrained chelating ligands are best avoided, in particular complexes with dppe considering that Ph substitution also does not help to activate M(0) centres to oxidative addition. Other parameters, such as the dihedral angle between two diphosphine ligands in Rh and Pd hydride complexes, were seen to be more significant than bite angle in determining the hydride donor ability of these complexes, which again could be a feature of differing steric bulk.[47, 48] The origin for bite angle effects in metal complexes therefore may have several different origins.[15, 49]

## Diphosphorus ligands with a single atom linker

Dppm is the archetypal diphosphine ligand with a single atom linker and can form a 4-membered chelate ring or act as a bridging ligand.[50, 51] The synthesis of both dppm and dppe was reported in 1959,[52] and coordination studies with group 6 carbonyls were reported shortly afterwards in 1960.[53] Dppm has one of the smallest natural bite angles ($\beta_n$), as calculated by molecular mechanics using a 'dummy' atom that directs the lone pairs of the bidentate ligand to point towards it without the electronic properties of the metal artificially influencing the bite angle.[4, 54] Heavier group 15 derivatives, such as $Ph_2AsCH_2AsPh_2$ and $Ph_2SbCH_2SbPh_2$, are known[50] but are currently not important ligands in catalysis.

Dppm, and analogues,[55] have a number of binding modes including chelating (**I**, Scheme 4), mono-nuclear mono-dentate (**II**, related to **I** by de-coordination of one donor), dinuclear complexes with well separated metal centres (**III**) or bridged dinuclear complexes with the metals constrained to be close together (**IV** and **V**). 'A-frame' complexes contain bridging dppm ligands as before, but the emphasis here is placed on the additional bridging ligand that is enforced by the close proximity of the metal centres.[50, 56]




**Scheme 4**. Binding modes for dppm and related ligands.

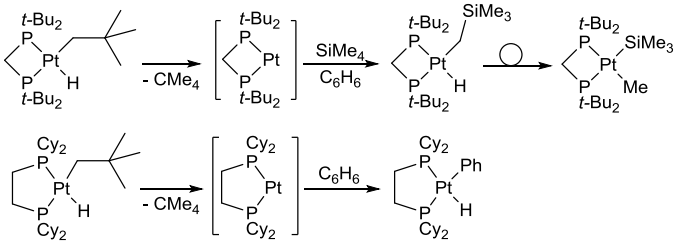
### Effect of the linker

Changing the linking unit, E, can have many effects. For instance, dppm can be deprotonated by strong bases to produce the corresponding anion,[51] so mono-substitution of the methylene backbone (readily achieved through lithiation and reaction with an electrophile)[57-59] has been used to slow down the rate of deprotonation.[60] Disubstitution of the methylene backbone would presumably inhibit deprotonation altogether, however, disubstitution of the backbone has mainly been investigated for another reason; the Thorpe-Ingold, or geminal-dialkyl,[61, 62] effect that leads to the widening of the angle between the two bulky geminal substituents on the backbone and compression of the other bond angles (Scheme 4). This leads to more favourable cyclisations and therefore better chelating ligands.[59] The use of large substituents on the phosphorus atoms also has the same effect.[63] On the other hand, the Thorpe-Ingold effect has been shown to inhibit rates of reductive elimination precisely by stabilising the chelate ring and suppressing favourable reductive elimination pathways via low coordinate intermediates.[64]

Changing the linker from $CR_2$ to N-R has led to a series of bis(phosphino)amine (also known as diphosphazane) ligands which have been very successful in catalysis.[65-68] Potential reasons for this success include the trigonal planar nitrogen atom[69] (resembling $sp^2$ hybridisation), their resistance to deprotonation and the enhanced electronegativity of nitrogen. Over the past 15 years, many PNP ligands have been synthesised and tested in ethene oligomerisation (see section below). Although this has allowed tends in what makes a productive catalyst to be identified,[70] the relative influence of steric and bite angle effects on individual reaction steps (such as reductive elimination etc) has not been deduced. One example of this is that although reduced steric bulk on the P-donors is associated with improved 1-octene selectivity, secondary alkyl substituents on the N atom also improves catalyst performance compared to the smaller Me substituent.[71] $sp^2$ hybridisation of the linker can also be achieved with carbon as in 1,1-bis(diphenylphosphino)ethene (vdpp, Figure 1),[72] or through incorporation of one phosphorus donor as part of a phosphinine ring.[73] $R_2POPR_2$ ligands (diphosphoxanes) are only stable with electron-withdrawing substituents due to facile rearrangement to $R_2P\text{-}P(=O)R_2$,[66] and have not been widely used in catalysis.

### Effect of the phosphorus substituents

Phosphine donors with aryl, or even better alkyl, substituents are considered to be good σ-donors and form strong bonds to most of the transition metals, and particularly to the late TMs. Alkyl groups have the effect of making the P donors more electron rich and therefore better σ-donors, increasing the electron density on the TM. Combining this enhanced σ-donation with steric bulk (favouring chelating complexes) led to Pt(0) complexes that reacted with $SiMe_4$ to generate the Si-C oxidative addition product (Scheme 5).[74] Calculations had suggested that decreasing the bite angle of the ligand would enhance reactivity due to a higher energy HOMO (Figure 2),[37] but no C-H activation of benzene was observed unlike for $[Pt\{P(Cy)_2C_2H_4P(Cy)_2\}]$.[75, 76] The reasons behind this surprising selectivity for $SiMe_4$ activation are still not clear.[77]




**Scheme 5**. Pt(0) diphosphine complexes in bond activation reactions.

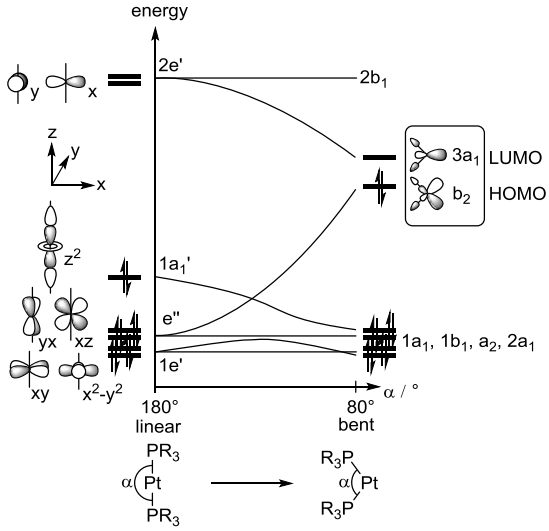



**Figure 2**. Walsh diagram for a 14-electron $d^{10}$ fragment as a function of the L-M-L angle when distorted from linear to bent, adapted from the literature.[37, 78, 79]

The use of other substituents that could lead to π-accepting properties, such as OR or OPh,[80, 81] has been significantly less well explored despite the potential for new reactivity utilising π-accepting P donors. Unsymmetrical $P(R)_2CH_2P(R')_2$ ligands are known.[82, 83] Incorporating π-accepting pyrrolyl substituents[84] or the aromatic and π-accepting phosphinine[85] moiety into a small bite angle ligand has been achieved,[73, 86, 87] along with other exotic P moieties such as phosphole (Figure 3).[88, 89] Having two

electronically differentiated donors on a chelating ligand has been termed a 'hybrid ligand', where hemilability, *trans*-influence or other electronic factors can be used to increase the complex's reactivity or selectivity.[90]

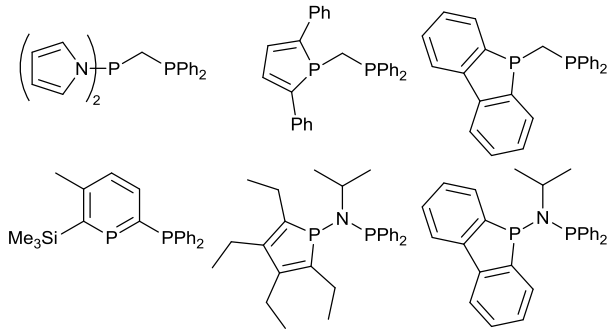


**Figure 3**. Hybrid ligands with single atom linkers.

Chiral bidentate phosphines containing a methylene linker have been synthesised by deprotonation of $RP(BH_3)Me_2$ (R = $^i$Pr, Cy, $^t$Bu, Ph) using *s*-BuLi and (–)-sparteine as a chiral ligand, followed by reaction with $RPCl_2$ and then subsequent reaction with MeMgBr.[91] The $BH_3$-protected (*R*,*R*)-P(R)(Me)$CH_2$P(R)(Me) enantiomers were then separated from the achiral *meso* forms by recrystallisation in 13 – 28% yield.[91] They have been given the abbreviation MiniPHOS due to the single atom in the backbone.[91] The *C*$_1$ symmetric P($^t$Bu)$_2$$CH_2$P($^t$Bu)Me has also been synthesised and resolved using preparative chiral HPLC,[92] and the applications of these and other chiral ligands in catalysis will be discussed below (Figure 4).

**Enhanced stabilisation of specific binding modes and geometries**

A combined theoretical and experimental investigation into Ni(0) ketene binding showed a dependence of the binding energy on the diphosphine ligand bite angle.[93] The metal-centred $b_2$ orbital is the HOMO (Figure 2), and this was found to preferentially interact with the C=O π* orbital (which is lower in energy than the C=C π* orbital).[93] The energy preference for η$^2$-CO binding was found to increase with decreasing bite angle driven by the increasing energy of the HOMO as the bite angle decreases.[37] This preference was experimentally confirmed by structural determination of the CO binding mode by X-ray crystallography.[93] The effect of changing dppm for dppe in seven coordinate W precatalysts for ROMP has been probed computationally (Chart 1).[94] Whilst the dppm complex has been crystallographically characterised, the dppe analogue was unknown.[94] Computational chemistry predicted that binding energies for *all* of the ligands decreased in the dppe complex because of the extra steric strain from the Ph substituents brought about by the wider bite angle dppe ligand.[94]

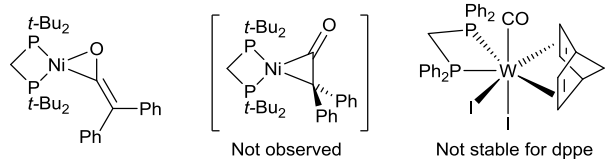
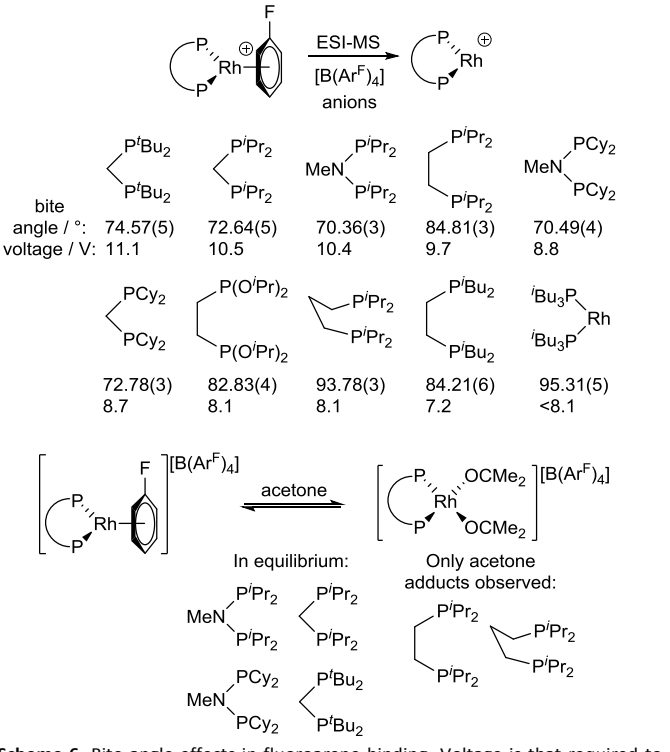



**Chart 1**. Stabilisation of different ligand and metal geometries.

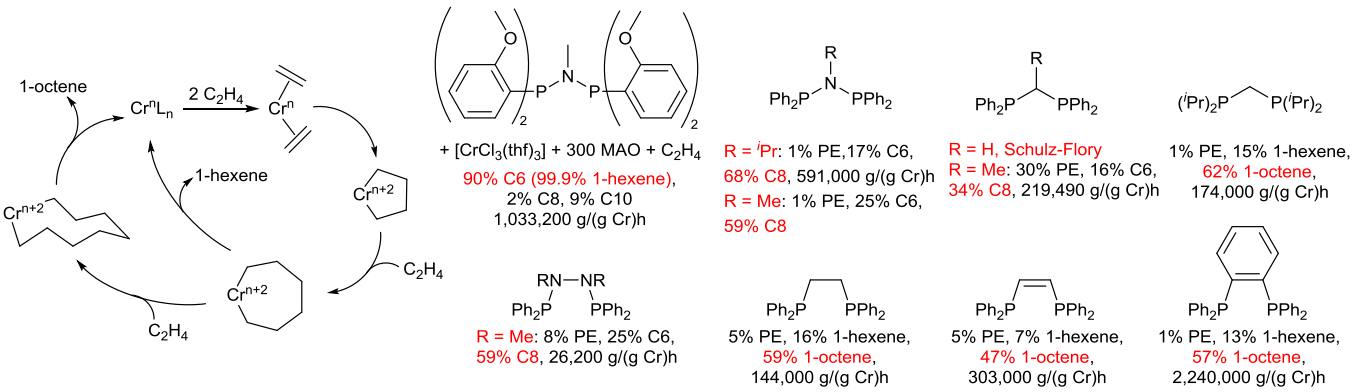
The influence of bite angle on binding of fluoroarenes[95] has been probed using electrospray ionisation mass spectrometry by applying a varying capillary exit voltage to give different degrees of fragmentation.[96] The voltage that gives 50% fragmentation can thereby give a qualitative indication of the strength of the binding of the fluorobenzene ligand where a higher voltage indicates a more strongly bound ligand. Comparing the series $^i$Pr$_2$P(CH$_2$)$_n$PPr$^i_2$, the binding energy increases with decreasing n (linker length), which correlates with decreasing bite angle.[95] The trend does not exclusively follow bite angle because stabilisation of the putative 2-coordinate Rh centres will be different with different phosphine substitution (from agostic interactions *etc.*), and steric effects from the P substituents also have a role to play. The values for NMe versus $CH_2$ backbones are almost identical, despite PNP ligands having the smaller bite angles.[96] Previous studies have shown that dissolving fluorobenzene adducts in acetone gave different products depending on the bite angle of the diphosphine ligand.[97] Complexes with 4-membered chelate rings showed an equilibrium between fluorobenzene and acetone adducts, whereas larger chelate rings gave exclusively the acetone adducts.[97] This is in agreement with the previous finding of stronger arene binding with narrower bite angle.




**Scheme 6**. Bite angle effects in fluoroarene binding. Voltage is that required to induce 50% fragmentation to the arene-free species. Ar$^F$ = 3,5-(CF$_3$)$_2$C$_6$H$_3$.

**Hemilability**

Coined in 1979,[98] the term hemilabile is given to a polydentate ligand with two different donors where one donor is bound more weakly than the other(s) and can readily dissociate. However, the ring strain in dppm complexes with a 4-membered chelate can also lead to dissociation of one donor arm acting like a hemilabile ligand (**I** to **II**, Scheme 4).[99] A




**Scheme 7**. Cr catalysed ethene oligomerisation and key $R_2PEPR_2$ ligands with the product distribution and catalyst productivity (the major product is emphasised in red).

pertinent example was demonstrated from the crystallisation of [Ru(*p*-cymene)$Cl_2$(dppm)] which gave the ionic $\kappa^2$-dppm complex from MeOH or the $\kappa^1$-dppm complex from acetone.[100]

## Applications in catalysis: transformations of alkenes

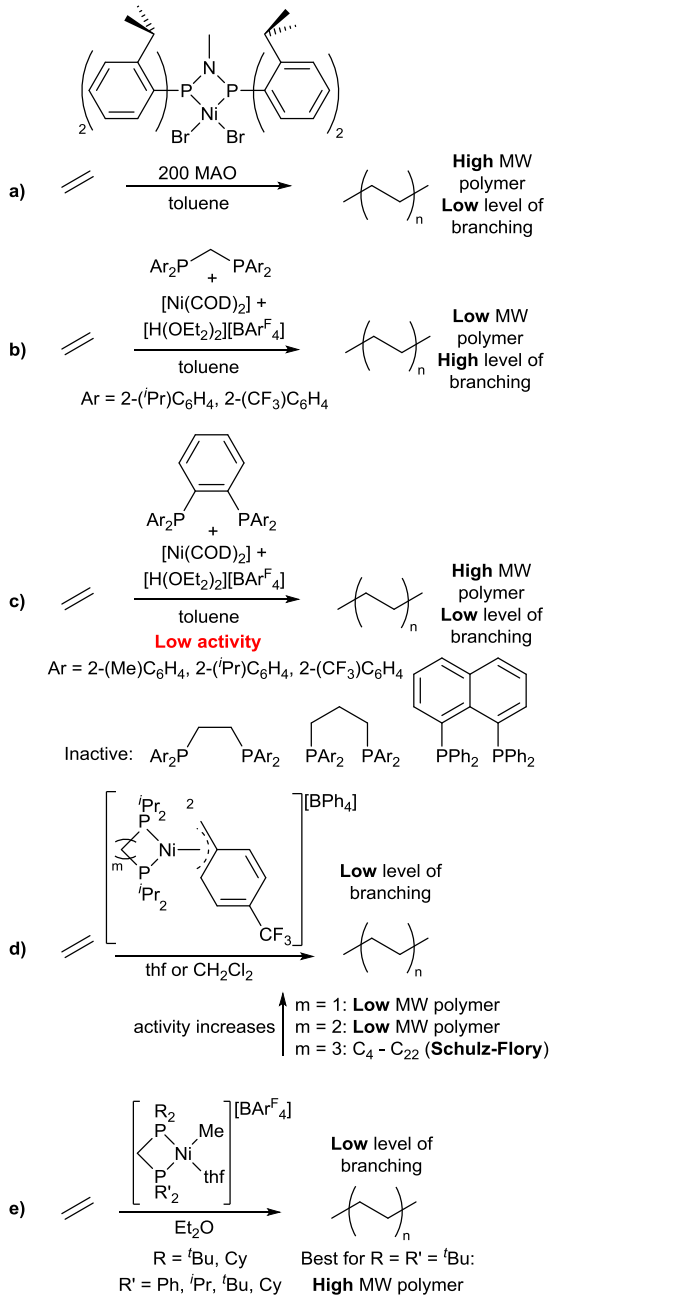
The use of dppm, and other single-atom linked diphosphorus ligands, is very widespread throughout the literature. Therefore, two main topics – that represent the most important uses of these ligands – have been focused on for this perspective: transformations of alkenes (including oligomerisation, polymerisation, copolymerisation and hydrogenation) and transfer hydrogenation / hydrogen-borrowing reactivity. A handful of other specific examples will be discussed as well. Although not comprehensive, these examples show key similarities helping to identify parameters that make for successful ligands.

### Ethene tri- and tetramerisation

The short chain terminal alkenes 1-hexene and 1-octene are important co-monomers for the production of low-density polyethylene (LDPE), and have other applications as well.[70, 101] Therefore, the development of selective oligomerisation processes for ethene has been a commercially important development because it offers key advantages over non-selective processes delivering Schulz-Flory or other non-selective distributions of products (such as the Aufbau reaction or Shell Higher Olefin Process).[70, 71, 101, 102] Several systems have now been developed for selective oligomerisation using chromium and pyrrolyl, triazacycloalkane or small bite angle PNP ligands.[102] A highly distinctive metallacyclic mechanism has been attributed as the reason behind high selectivities, with expansion of a 5-membered metallacycle to either a 7- or a 9-membered metallacycle driving the selectivity towards 1-hexene or 1-octene respectively (Scheme 7).[103] The first report of a PNP catalyst demonstrating ethene trimerisation was in 2002.[104, 105] This catalyst is extremely active (TOF > 1.8 x $10^6$ $h^{-1}$ at 20 bar)[106] and selective to 1-hexene (90%). Removing the *ortho*-substituents on the aryl groups leads to more space around the metal centre (and removes any potential coordination of the *ortho*-OMe donors) giving rise to up to 70% 1-octene formation (NR = N$^i$Pr$_2$), along with 1-hexene.[107, 108] These tetramerisation catalysts retain high levels of activity (TOFs up to 1.1 x $10^6$ $h^{-1}$)[106] and productivity, but 45 bar of ethene was required to demonstrate productive tetramerisation, as opposed to trimerisation which can be achieved at the lower pressure of 1 bar.[70, 104, 107] These exceptional catalysts already highlight the importance of the nature of the aryl and nitrogen substituents emphasising the important effects steric bulk has on catalysis. The nature of the backbone is important as well because changing the ligand to dppm revealed a dramatic shift to a non-selective Schulz-Flory product distribution; vdpp was even less active and also unselective.[109] Alkyl substitution of the methylene backbone was found to restore some selectivity to the oligomerisation (ca. 34% yield of C8), but high levels of polyethylene were also formed and at lower productivities.[60] The direct comparison between C(H)Me and NMe reveals the clear superiority of the PNP ligand framework. Interestingly, moving to wider bite-angled diphosphines with $C_2$ linkers restored catalyst performance, with the ligand featuring a 1,2-disubstituted benzene backbone giving an extremely active catalyst,[109] more so than for a PNNP ligand.[107] Performance and selectivity dropped again upon widening the bite angle using dppp.[109] P($^i$Pr)$_2$CH$_2$P($^i$Pr)$_2$ also gave an effective catalyst for ethene tetramerisation, indicating that if ligand non-innocence can be avoided, then small bite angle ligands with a $C_1$ backbone can be useful.[109] Pringle and co-workers attempted to incorporate the bicyclic phobane (Phob) moiety into both symmetrical and unsymmetrical PNP ligands, but due to the large steric bulk of phobane, the symmetrical PhobN(Me)Phob proligand was not isolated.[110] Unsymmetrical variants with $PPh_2$ and P(*o*-tolyl)$_2$ donors were successfully synthesised, and testing in Cr catalysed ethene oligomerisation revealed high polymer formation (11 and 43 wt% respectively), yet still achieving high 1-octene to 1-hexene ratios in the liquid fraction.[110] The effect of bite angle is clearly intertwined with other factors including P substituents, backbone unsaturation, backbone stability and backbone rigidity, but it can be generally concluded that smaller bite angles lead to higher 1-octene:1-hexene ratios.[109] Catalysts with hydrocarbon-linked diphosphine ligands can be successful, but do not exceed the excellent selectivities achieved with the best PNP ligands.

**Ethylene polymerisation**

Brookhart and co-workers described highly active Ni catalysts that were capable of polymerising ethene and terminal alkenes to high molecular weight polymers in 1995.[111] These α-diimine catalysts sparked renewed interest in both late transition metal and first row transition metal polymerisation catalysis.[112, 113] PNP ligands for use in Ni polymerisation catalysis were described in 2001. *ortho*-$^i$Pr substitution on the aryl substituents gave highly active catalysts, with steric blocking of the Ni centre's axial coordination sites considered to be essential to stop chain transfer (Scheme 8, **a**).[69] PNP catalysts with *ortho*-$OMeC_6H_4$ substituents gave similar results.[114] Dppm-analogues with *ortho*-aryl substitution instead gave catalysts that produced low weight and highly branched polyethylene (PE), in contrast to the PNP complexes (Scheme 8, **b**).[115] Whereas Ni complexes of flexile $C_2$ and $C_3$ linked diphosphines were inactive, 1,2-disubstitued benzene derivatives gave catalysts that yielded PE with similar properties to the PNP ligands, albeit with low activity (Scheme 8, **c**).[115] It can be concluded that steric protection of the metal by *ortho*-aryl substitution was important and that small bite angles favoured the production of active catalysts. One possible explanation is that small bite angles would tend to favour square planar Ni(II) over inactive tetrahedral Ni(0), and as rigid backbones were also found to be useful, these ligands might be active for the same reason.[115]

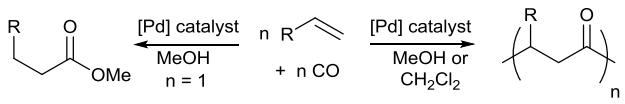



**Scheme 8**. $R_2PEPR_2$ ligands for use in Ni catalysed ethene polymerisation.

Cationic Ni benzyl complexes with $(^iPr)_2P(CH)_mP(^iPr)_2$ ligands were tested for ethylene polymerisation (Scheme 8, **d**), and the most active catalyst was generated with m = 1 that produced low MW polymer.[116] Widening the bite angle caused a significant decrease in activity and for m = 3, only oligomers were formed.[116] However, increasing the size of the P substituents to $^t$Bu succeeded in producing very active catalysts that gave high molecular weight, straight chain PE, and the trend of greater steric bulk leading to increased polymer length was found (Scheme 8, **e**).[117] Overall, the general trends found for Ni polymerisation catalysts mimic those drawn from Cr trimerisation studies where small bite angle ligands (as well as rigid ligands) are favourable, and the substituents on the P donors are important for controlling the product distribution.

**Polyketone**

Co-polymerisation of CO and alkenes produces 'polyketones' (Scheme 9), polymers with some exceptional properties.[118, 119] In contrast, the reaction of one molecule of CO with one equivalent of alkene and MeOH leads to methoxycarbonylation, which yields methyl propanoate from ethene and has become a very important industrial process in the production of methyl methacrylate.[120] Both ligand bite angle and nature of the phosphorus donors are important factors in governing the product distribution. Early research showed that Pd dppp catalysts gave the highest rate for polyketone formation and produced the highest MW polymers with the rate decreasing dppp > dppb > dppe; Pd dppm complexes found to be inactive.[118] When comparing the effect that the P substituents have, it was shown that Pd complexes of the strongly σ-donating ligands 1,2-{$CH_2P(^tBu)_2$}$_2C_6H_4$ and $P(^tBu)_2(CH_2)_3P(^tBu)_2$ gave methyl propanoate with extremely high selectivities,[120] whereas dppp and 1,2-{$CH_2P(Ph)_2$}$_2C_6H_4$ gave perfectly alternating polyketone.[118, 121, 122] Clearly, the nature of the P donors is very important in addition to the bite angle.




**Scheme 9**. Methoxycarbonylation versus polyketone formation with CO/alkenes.

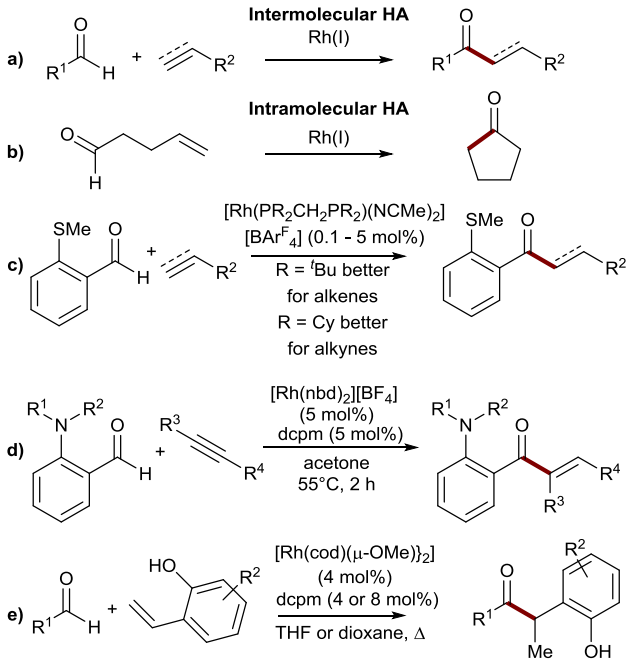
Pd complexes of $Ar_2PCH_2PAr_2$ ligands were made into highly active polymerisation catalysts by increasing the steric bulk of the Ar substituents, with *ortho*-$^i$Pr substituents giving a five-fold rate enhancement compared to *ortho*-Et.[123] Dppm has a high tendency to bridge between two square-planar metal centres, so additional steric bulk on the aryl substituents could help direct the formation of a chelating complex thereby generating an active *cis*-coordinated catalyst.[124] $Ar_2PN(Me)PAr_2$ analogues were also tested and the same trend was found with the *ortho*-$^i$Pr derivative found to be the most active, and even more active than dppp under the same conditions.[123] Results from the patent literature showed that Pd(II) complexes with $(^tBu)_2PCH_2P(^tBu)_2$ lead to effective catalysts for CO and ethene copolymerisation yielding high-molecular-weight polyketones,[117, 125, 126] again emphasising the importance of sterically bulky P substituents.

**Hydroacylation**

Hydroacylation is the formal insertion of an alkene (or alkyne) into the C-H bond of a formyl (RC(O)H) unit transforming an aldehyde into a ketone (Scheme 10, **a**). The reaction is usually catalysed by homogeneous Rh catalysts and is an atom-economic methodology for C-C bond formation that is gaining increasing interest in the literature.[127] Early studies showed the beneficial properties of chelating diphosphine ligands over the marginally active $[Rh(PPh_3)_3Cl]$ for the conversion of 4-pentenals to cyclopentanones (Scheme 10, **b**), with $[Rh(dppe)(solvent)_2]^+$ giving between 100 to 800 turnovers before formation of carbonylated Rh species slows the catalysis.[128, 129] The reductive elimination of the ketone has been assigned as the rate determining step,[130] so more productive catalysts were sought that could perform this reductive elimination more quickly reducing the amount of carbonylated species. Willis, Weller and co-workers have investigated the use of both the wide bite angle DPEphos ligand,[131] which can potentially bind $\kappa^1$, $\kappa^2$ or $\kappa^3$,[35] as well as sterically bulky small bite angle $R_2PCH_2PR'_2$ (R, R' = Cy, $^t$Bu) ligands in order to probe whether small bite angles and large steric bulk would help increase the rate of reductive elimination of the ketone. The successful use of both very wide and very narrow bite angle ligands for the same catalytic reaction is an intriguing observation, and it is not clear whether a single property common to both, e.g. increased rates of reductive elimination through dissociation of one P donor atom,[35, 132] is important or whether they are successful for different reasons, e.g. steric crowding.[133, 134] For DPEphos, it has also been suggested that $\kappa^3$ coordination inhibits decarbonylation (the competing detrimental process).[35] With judicious choice of solvent and substrate/catalyst concentrations, decarbonylation could be avoided so that low catalyst loadings were achieved using the beneficial properties of the small bite angle and strongly σ-donating ligands (Scheme 10, **c**).[130] A subsequent comparison of $P(^iPr)_2(CH_2)_nP(^iPr)_2$ based Rh catalysts showed that the catalyst with n = 2 was a very fast catalyst for the hydroacylation of octyne, better than for n = 1 and almost as good as the best catalyst which is a PNP derivative $P(^iPr)_2N(Me)P(^iPr)_2$.[97] The similar PNP catalyst $PCy_2N(Me)PCy_2$ was subsequently found to be advantageous giving better regioselectivity for the intermolecular hydroacylation of propargylic amines.[135] For the most challenging internal alkenes, an unsymmetrical catalyst bearing a $P(^tBu)_2CH_2P\{o\text{-}(OMe)C_6H_4\}_2$ ligand was found to be the most active.[133] These results suggest that although a general identification of the structure of the best catalyst is possible, for individual reactions, some level of catalyst screening is still required to find the perfect match. Rh-catalysed hydroacylation of alkynes with 2-aminobenzaldehyde derivatives (Scheme 10, **d**) showed that the rate decreased in the following order: $P(Cy)_2CH_2P(Cy)_2$ (dcpm) >> dppm > dppe > dppp,[136] and the hydroacylation of vinylphenols (Scheme 10, **e**) showed a similar trend with dppm less active than dcpm. Wider bite angle phosphines were completely ineffective.[137] Mechanistic studies on the hydroacylation of vinylphenols identified a mixture of on- and off-cycle species in solution, but here oxidative addition of the aldehyde C-H bond was determined to be rate limiting.[46] The size of the ligand was also found to be important with $P(^tBu)_2CH_2P(Me)(^tBu)$ (Tcfp, Figure 4) not producing an active catalyst.[46] The authors proposed that the small bite angle dcpm ligand must favour oxidative addition (opposite to the trend described in the introduction for oxidative addition of $H_2$ to $[Rh(diphosphine)_2]^+$ complexes).[44, 45] However, the smaller cone angle for dcpm compared to Tcfp is at least consistent with observed reactivity only for the smaller ligand as the reaction produces a sterically crowded oxidative addition product. The more electron-rich dcpm ligand was faster than dppm. Their results contrasted with previous work[130] which indicated that small bite angles would favour rate limiting reductive

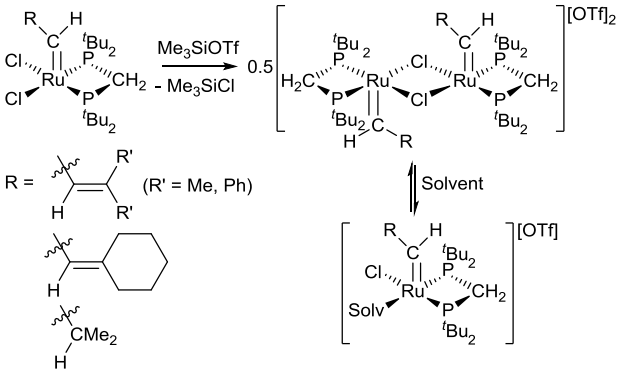
elimination, so mechanisms of hydroacylation may differ according to the substrate. Dppm[138] and dppe[139] were successfully used as ligands in Rh catalysed alkyne hydroacylation and conjugate addition sequences. Because the second step has different ligand requirements, the ligand has to be a compromise capable of working with both steps, or at least must not interfere with the second step.




**Scheme 10**. Hydroacylation (HA) catalysis. dcpm = $Cy_2PCH_2PCy_2$.

### Olefin metathesis

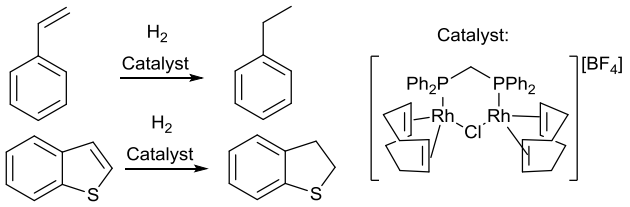
Grubbs' first generation Ru olefin metathesis catalyst features *trans*-phosphine and *trans*-chloride ligands in a square-based pyramidal structure with the carbene ligand at the apex.[140] Using $P(^tBu)_2CH_2P(^tBu)_2$ as the ligand, Hofmann and co-workers synthesised Ru carbene complexes with *cis*-phosphine donors, enforced by the narrow bite angle of the ligand, and with *cis*-Cl ligands.[140, 141] Although they acted as catalysts for the ROMP of norbornene, they were slower than other Ru(II) complexes.[140] However, upon addition of $Me_3SiOTf$, cationic catalysts with very high activity for ROMP were achieved (Scheme 11), and were found to be more active than Grubbs' first generation catalyst for the ROMP of cyclooctene.[141]




**Scheme 11**. Cationic olefin metathesis catalysts with a small bite angle ligand.

### Hydrogenation

Wilkinson's catalyst, $[Rh(Cl)(PPh_3)_3]$, is still the most popular homogeneous catalyst for hydrogenation reactions.[2] In square planar Rh(I) complexes, dppm acts as a bridging ligand.[50] Dinuclear Rh 'A-frame' dppm catalysts have been identified as catalysts for the homogeneous hydrogenation of alkenes and alkynes, although without any obvious advantages over Wilkinson's catalyst.[142, 143] A cationic dirhodium complex with only one bridging dppm ligand, and COD (cyclooctadiene) as the coligands, was screened for styrene hydrogenation catalysis, and compared with $[Rh(Cl)(PPh_3)_3]$ and $[Rh(COD)(PPh_3)_2][BF_4]$ (Scheme 12). All catalysts showed similar activities and the same excellent selectivity for ethyl benzene over other potential products displaying reduction of the aromatic ring.[144] However, for the hydrogenation of benzo[*b*]thiophene, a major contaminant and poison for heterogeneous catalysts present in fossil fuels, the dirhodium catalyst was found to be the most active and the most selective catalyst, better resisting competing C-C bond forming processes with the solvent at high temperature when compared to eight precious metal catalysts including Wilkinson's catalyst.[144] The enhanced selectivity could be due to the dinuclear core that restricts the binding mode of the substrate.[144] Coordination of the hybrid ligands P(phospholyl)$CH_2PPh_2$ (Figure 3) with $[\{Rh(COD)(\mu\text{-}Cl)\}_2]$ / $AgBF_4$ or $[Rh(COD)_2][OTf]$ gave a mixture of heteroleptic $[Rh(diphosphine)(COD)]^+$ and homoleptic $[Rh(diphosphine)_2]^+$ complexes, neither of which could be isolated pure.[88] However, using an in-situ method of combing the ligand, $[Rh(COD)_2][OTf]$ and substrate, catalytic homogeneous hydrogenation of methyl 2-(acetamidomethyl)acrylate (Scheme 13) was observed, with the diphenylphosphole ligand superior to the dibenzophosphole.[88]




**Scheme 12**. μ-dppm as a ligand in Rh hydrogenation catalysis.

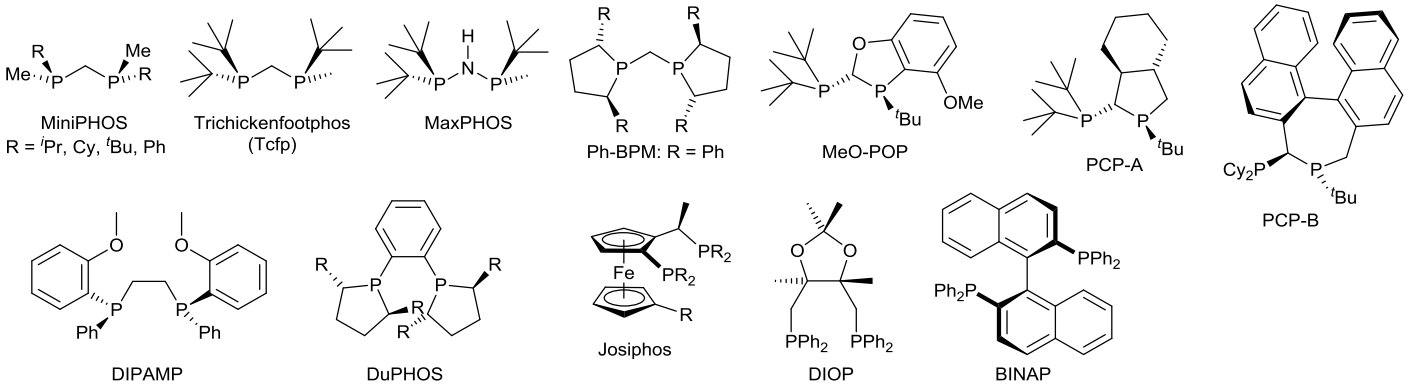
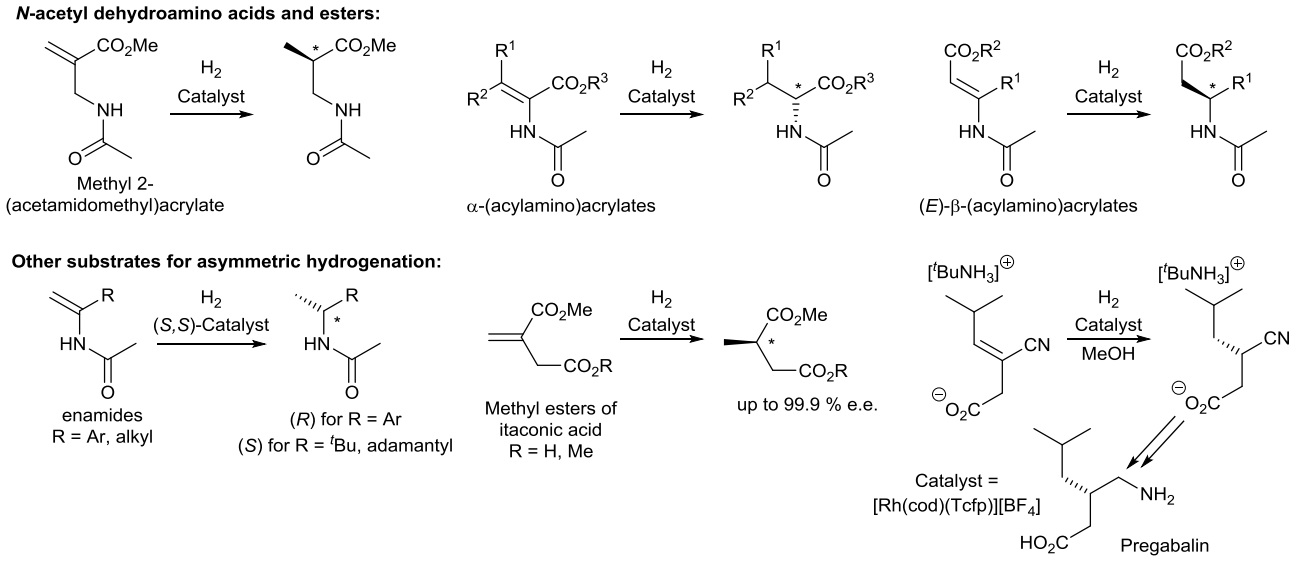



**Figure 4**. Chiral diphosphine ligands used in asymmetric homogeneous hydrogenation catalysis.

Most of the recent developments in homogeneous hydrogenation catalysis have focused on the industrially important area of asymmetric hydrogenation.[2] Historically, chelating bidentate phosphorus ligands have dominated the field, although monodentate ligands have made an important resurgence since 2000.[2] Although C2 linked diphosphines, such as DIPAMP and DuPHOS, or wider bite angle diphosphines, such as Josiphos (C3), DIOP (C4) or BINAP (C4), are often used, several classes of C1-linked chiral diphosphine ligand have also been developed (Figure 4, top).

MiniPHOS is P-chirogenic[145, 146] and also $C_2$ symmetric following a common design principle for chiral diphosphines that block two of the diagonal quadrants when the space around the metal centre is divided up in this fashion.[147, 148] The C1 linker was investigated because rigid backbones (such as in DuPHOS) have been implicated in achieving better enantioselectivities, while electron donating alkyl substituents increase catalytic activities giving access to a larger number of substrates.[149] Only homoleptic $[Rh(miniPHOS)_2]^+$ complexes could be isolated with these ligands,[91, 149] but these complexes still achieved high enantioselectivities for the hydrogenation of functionalised alkenes.[91, 149, 150] NMR spectroscopic studies showed that $[Rh(miniPHOS)_2][BF_4]$ reacts with hydrogen at low temperatures to make the octahedral *cis*-dihydride which isomerises to the *trans*-dihydride at around -20°C via reversible decoordination of one P donor, a process that was suggested to also be important in binding a substrate prior to hydrogenation.[151] Comparison of $[Rh(miniPHOS)_2][BF_4]$ catalysts with the C2 linked $[RhP(^tBu)(Me)C_2H_4P(^tBu)(Me)(NBD)]^+$ (NBD = norbornadiene) for the hydrogenation of dehydroamino acids and esters (Scheme 13) revealed that although miniPHOS complexes were slower catalysts (likely due to the slower reaction of the bis(diphosphine) complex), extremely high enantioselectivities of up to 99.9% could be achieved.[151, 152] However, for the hydrogenation of enamides, the related ligand with a C2 linker was found to be superior,[150] whereas for hydrogenations of (*E*)-β-(acylamino)acrylates, there was little difference between the two.[153]

Trichickenfootphos (Tcfp), as named by the workers who developed it based upon a visual inspection of the $^t$Bu substituents, blocks three quadrants as opposed to MiniPHOS that blocks two. Unlike with MiniPHOS, cationic heteroleptic $[Rh(diphosphine)(diene)]^+$ complexes were readily synthesised and this complex was found to give near perfect selectivities for




**Scheme 13**. Asymmetric hydrogenations.

the enantioselective hydrogenation of five α-acetamido dehydroamino acids,[92] as well as excellent e.e.s for β-acetamido dehydroamino acids[154] and other substrates.[155] The complex was also tested for the enantioselective hydrogenation of an intermediate on the way to pregabalin (Scheme 13), a pharmaceutical used to treat epilepsy and nerve pain, and its performance was superior to Me-DuPHOS because the reaction could be run at twice the concentration, and with a 10 fold reduction of catalyst loading giving 98% e.e. on 100 g scales.[92] The PNP analogue MaxPHOS has been developed,[156-158] and [Rh(MaxPHOS)(COD)][X] complexes were synthesised, as for Tcfp. X-ray crystallography revealed a smaller bite angle of 70.0° for MaxPHOS compared to Tcfp (72.6°).[156] CO stretching frequencies for their [Rh(diphosphine)$(CO)_2$][$BF_4$] complexes, as well as $^{77}$Se coupling constants for the corresponding diphosphine selenides, reveal that MaxPHOS is a slightly less electron rich ligand than Tcfp as expected from the more electronegative N backbone.[158] Its use in catalytic asymmetric hydrogenation revealed that it is also an excellent ligand producing high e.e.s.[156, 158] The C1-linked analogue of DuPHOS (Ph-BPM, Figure 4) has been synthesised and its Rh complexes gave excellent activity and selectivity for the asymmetric hydrogenation of dimethyl itaconate and dehydroamino acids.[159] MeO-POP, PCP-A and PCP-B (Figure 4) are additional $C_1$ symmetric chiral ligands that have been shown to be useful in the asymmetric Rh catalysed hydrogenation of α- and β-(acylamino)acrylates.[160-162] These ligands also proved to be useful for Co[163] and Rh[164] catalysed asymmetric Pauson-Khand reactions. In contrast to the P-chirogenic ligands, Rh complexes with $PR_2CH_2P$(menthyl)$_2$ ligands that bear chiral (1*S*,2*R*,5*S*)-menthyl substituents were only found to give moderate e.e.s in the hydrogenation of the methyl ester of α-acetamidocinnamic acid.[165]

## Catalysis using substrates other than alkenes

### Transfer hydrogenation

Transfer hydrogenation (TH) uses other chemical sources of hydrogen, such as isopropanol or formic acid, to perform reduction reactions instead of hydrogen gas.[166] This can lead to safer processes as it avoids the use of pressured and explosive gases, as well as more convenient synthetic methods. PNP ligands have been used in Ru and Rh catalysed transfer hydrogenation,[67] and complexes **A** – **F** (Figure 5) have demonstrated good conversion for the TH of acetophenone to PhC(OH)(H)Me, a standard substrate (Table 1), as well as substituted acetophenones. [167-171] Their advantages include being relatively resistant to air and water, but none of the catalysts were shown to work at room temperature or without base. *cis*-$RuCl_2$ complex **G**, with two phosphinophosphinine ligands, showed excellent catalytic activity upon activation with KO$^t$Bu for the room temperature transfer hydrogenation of acetophenone and a number of derivatives.[73] After 1 hour at 20°C, 94 % conversion of acetophenone was achieved, with higher conversions of *para*-Br (97 %) and *para*-F (96 %) acetophenone observed. *para*-Me (87 %).[73] *para*-OMe (48 %) and *para*-$NO_2$ (5 %) acetophenones gave lower conversions at 20°C, but these were increased upon heating at 82°C (98%, 79% and 72% respectively).[73] *ortho*-OMe acetophenone also went to completion upon heating at 82°C for 1 hour.

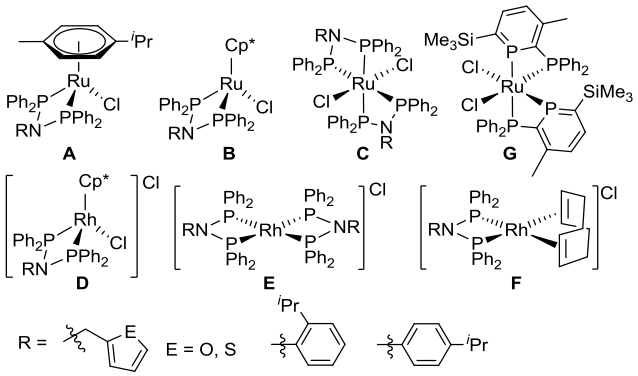



**Figure 5**. Ru (Top) and Rh (Bottom) TH catalysts.

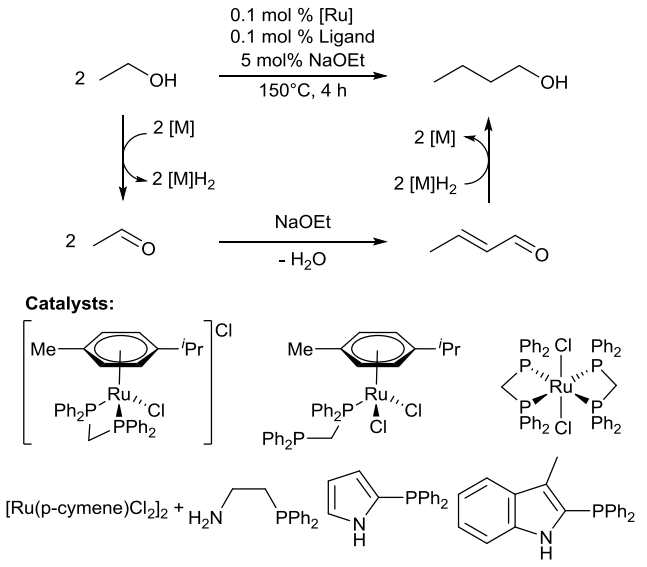
| Catalyst | N-substituent | Mol % cat. | Time | Conversion | Ref |
|---|---|---|---|---|---|
| **A** | $CH_2$-$C_4H_3S$ | 1 | 1 h | < 1 % | 167 |
| **A** | $CH_2$-$C_4H_3S$ | 0.1 | 1 h | 99 % | 167 |
| **A** | 2-$^i$Pr$C_6H_4$ | 0.1 | 2.5 h | 96 % | 168 |
| **A** | 4-$^i$Pr$C_6H_4$ | 0.1 | 4 h | 98 % | 168 |
| **B** | 4-$^i$Pr$C_6H_4$ | 0.1 | 32 h | 99 % | 168 |
| **B** | $CH_2$-$C_4H_3O$ | 1 | 6 h | 99 % | 169 |
| **B** | $CH_2$-$C_4H_3S$ | 1 | 6 h | 98 % | 169 |
| ***trans*-C** | $CH_2$-$C_4H_3S$ | 0.2 | 3.5 h | 99 % | 170 |
| **D** | $CH_2$-$C_4H_3O$ | 1 | 3 h | 99 % | 169 |
| **D** | $CH_2$-$C_4H_3S$ | 1 | 3 h | 98% | 169 |
| **E** | $CH_2$-$C_4H_3O$ | 1 | 1 h | 99 % | 171 |
| **E** | $CH_2$-$C_4H_3S$ | 1 | 1 h | 99 % | 171 |
| **E** | 2-$^i$Pr$C_6H_4$ | 1 | 1 h | 98 % | 171 |
| **E** | 4-$^i$Pr$C_6H_4$ | 1 | 1 h | 99 % | 171 |
| **F** | 2-$^i$Pr$C_6H_4$ | 1 | 10 min | 97 % | 171 |
| **F** | 4-$^i$Pr$C_6H_4$ | 1 | 5 min | 99 % | 171 |

**Table 1**. TH of acetophenone, PhC(O)Me. Conditions: refluxing $^i$PrOH; acetophenone/[Ru] catalyst/NaOH.

### Hydrogen-borrowing catalysis

Hydrogen-borrowing reactions involve a catalyst removing an equivalent of $H_2$ from a substrate in order to facilitate additional reactivity, before the 'borrowed $H_2$' is then returned.[172, 173] This process is most often applied to the activation of alcohols because the oxidised carbonyl compounds formed by hydrogen borrowing have a wide scope of reactivity.[174-176] This represents an important development because alcohols by themselves are relatively unreactive requiring pre-functionalisation into more reactive, and potentially more harmful, alkyl halides or sulfonates.[177] As with hydroacylation, both very wide and very narrow bite angle ligands have been applied in this catalysis. For example, DPEphos[178] and Xantphos[179, 180] ligands have been used in the Ru-catalysed hydrogen-borrowing amination of alcohols.[181] For small bite angle ligands, dppm has been the most widely applied diphosphine ligand in these processes, in contrast to many of the examples above where alkyl P-substituents were preferred, or more generally in homogeneous catalysis where longer linker lengths are usually utilised.

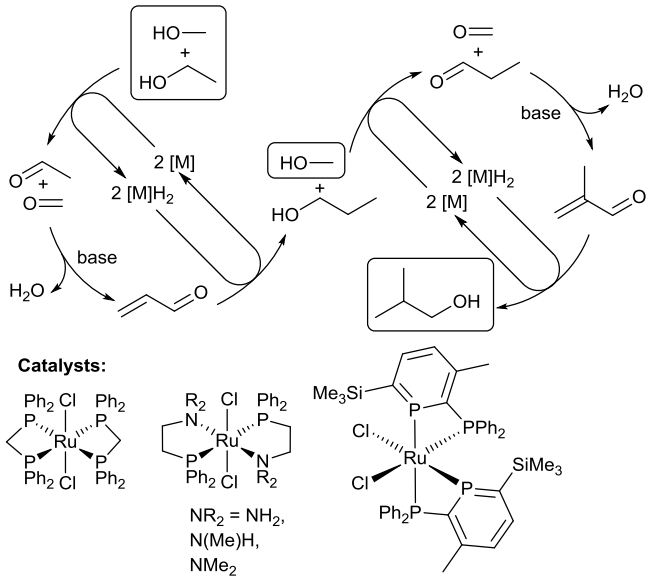
**Production of n-butanol** The Guerbet reaction has been known for many years,[182, 183] and is a hydrogen-borrowing process that produces a β-alkylated alcohol.[184] The mechanism involves the conversion of two equivalents of alcohol into the corresponding aldehydes, which dimerise in an aldol reaction, before hydrogen is transferred back to the unsaturated intermediate to generate a longer chain or branched alcohol (see Scheme 14 for EtOH).[184-187] Long chain alcohols have many uses including as fuels because they have a number of advantages over EtOH, which is hydroscopic and can be corrosive to current engine technologies.[184, 187, 188] A step-change in performance for EtOH to butanol catalysis[188] was demonstrated in 2013 using Ru/dppm catalysts (Scheme 14). Reactions with [{RuCl(η$^6$-*p*-cymene)(μ-Cl)}$_2$] and two equivalents of ligand (1:1 M:L ratio) showed dppm to be the best ligand with ethanol conversions of 20.4 % to n-butanol at 90% selectivity, almost double the conversions observed using dppe or dppp.[100] Preformed [RuCl(η$^6$-*p*-cymene)(dppm)]Cl performed slightly better with a higher conversion (22.1 %) and higher selectivity (93.6%), while the analogous complexes with dppe and dppp gave lower conversions. Complexes with two dppm ligands, such as *trans*-[Ru(Cl)$_2$(dppm)$_2$], were slower catalysts but more stable remaining in solution throughout the reaction and gave the highest conversion (48.5% after 24 hours).[100] The superior performance of dppm was recognised, and the involvement of hemilabilty was raised as a possible reason; the crystallographic identification of both κ$^2$-dppm and κ$^1$-dppm species when crystallised from MeOH or acetone respectively indicates facile dissociation of one donor.[100]




**Scheme 14**. n-Butanol formation using hydrogen borrowing catalysis.

A follow-up publication detailed the investigation of [P,N] ligands for *n*-butanol formation.[189] [{RuCl(η$^6$-*p*-cymene)(μ-Cl)}$_2$] and 1 or 2 equivalents of N(H)C$_2$H$_4$PPh$_2$ gave a catalyst with similar performance to dppm, along with 2-diphenylphosphinopyrrole, but the best performance was achieved using an indole-substituted phosphine (31.4% conversion, 92.7% selectivity).[189] However, the ligand was found to decompose during the catalysis to give foul-smelling 3-methylindole and hence was not considered promising for further development.

**Production of isobutanol** Isobutanol is termed an 'advanced biofuel' in comparison to the first generation biofuel EtOH as derived from food crops. Isobutanol is a useful fuel because it is more energy dense than EtOH, is less hydroscopic than EtOH and does not cause stress cracking in pipelines.[190] Isobutanol can be produced using homogeneous catalysis from two equivalents of MeOH and one equivalent of EtOH using hydrogen-borrowing methodology (Scheme 15).[191] [RuCl$_2$(dppm)$_2$] was again shown to be a superior catalyst to those with wider bite angle ligands giving higher conversions and selectivities (dppm: 66 % conversion, 98.1 % selectivity to isobutanol; dppe: 3% conversion, 95.4% selectivity; dppp: 5 % conversion, 59.2 % selectivity) over 2 hours reaction time (1 mL ethanol, 10 mL methanol, 0.1 mol % [Ru], 200 mol % base based on EtOH, 180°C). In comparison, the analogous catalysts using Ph$_2$PC$_2$H$_4$NR$_2$ [R$_2$ = Me$_2$, (Me)H, (H)$_2$] ligands are less active with decreasing performance upon mono- and dimethylation. Even so, the moderate activity with Ph$_2$PC$_2$H$_4$NMe$_2$ (31 % conversion, 93.2 % selectivity, 20 hours) demonstrates that an outer-sphere mechanism (substrate transformation without direct bonding to the metal centre) is not a requirement with these systems. The best system was found to be [RuCl$_2$(dppm)$_2$] at 180°C with a reaction time of 20 hours to give 75 % conversion to isobutanol with a selectivity of 99.8%, a stunning combination of high selectivity and conversion, and the proposed Guerbet mechanism was in agreement with $^{13}$C labelling studies.[191]

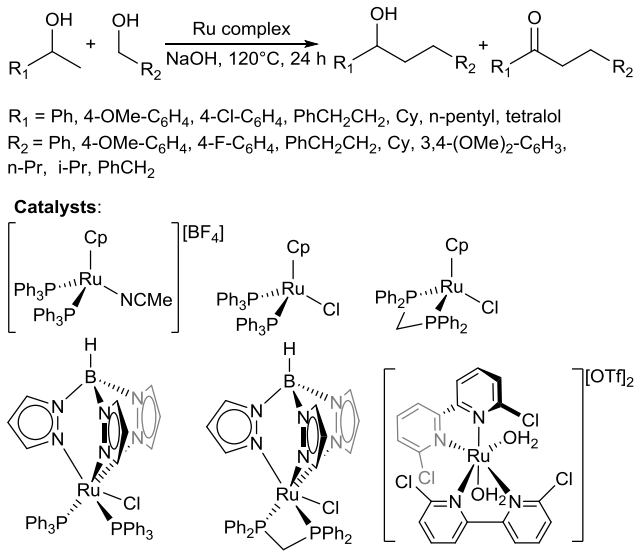



**Scheme 15**. Formation of isobutanol through consecutive hydrogen-borrowing cycles

A RuCl$_2$ complex with two 2-phosphinophosphinine ligands was also found to be a competent precatalyst for the formation of isobutanol from MeOH/EtOH in a hydrogen borrowing strategy.[73] Using the same conditions as above, a 35% yield of isobutanol was achieved (88% selectivity) in 2 hours, which was increased to 50% yield, 96% selectivity after 20 hours indicating

slower catalysis compared to dppm, but almost identical yields and selectivities to using the hybrid ligand $Ph_2PC_2H_4NH_2$.[73]

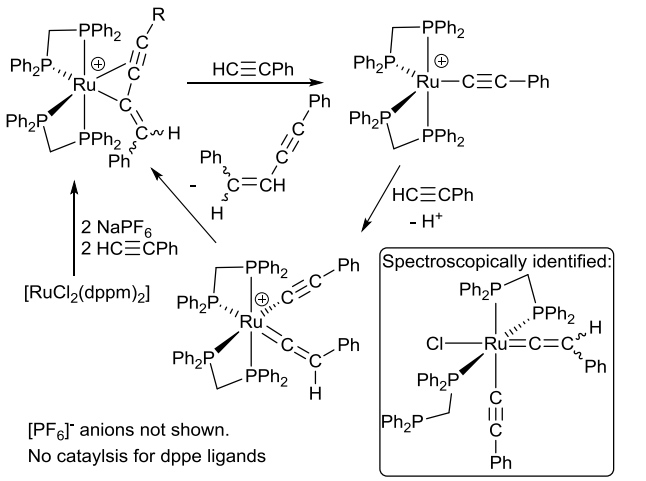
**β-alkylation of other alcohols** β-alkyation of secondary alcohols with primary alcohols[192] has been carried out using Ru catalysts containing dppm and $PPh_3$ co-ligands (Scheme 16).[193] For $R_1$ = $R_2$ = Ph, a slow background reaction was noted (formation of 11% of the product alcohol, 1% ketone), but adding any one of six Ru complexes catalysed the reaction forming between 71 % and 94% of the alcohol, 3 – 13 % ketone.[193] Although for this particular reaction [Ru(Cp)(dppm)Cl] gave the highest yield, overall a dichloro-bipy Ru complex (Scheme 16) was the most effective catalyst with the highest yields for most of the substrates tested. The reaction was also tested at 80°C, and [Ru(Cp)(dppe)Cl] was found to be a much poorer catalyst than $[Ru(Cp)(PPh_3)_2Cl]$,[194] indicating that again dppm is potentially a much better ligand than dppe for this reaction. At higher temperatures, $[RuCl_2(PPh_3)_2$(2-aminomethylpyridine)] was the best catalyst with 91 % yield in 5 hours.[194] In looking specifically at the effect of the small bite-angle dppm ligand compared to two $PPh_3$ ligands, the results were very similar,[193] indicating no systematic benefit to the small bite-angle chelating ligand.




**Scheme 16**. β-alkyation of secondary alcohols with primary alcohols.

**Hemilability of dppm and the dimerisation of alkynes**

Reactions of *cis*-$[RuCl_2(dppm)_2]$ with $NaPF_6$ and HCCPh demonstrated the formation of an $\eta^3$-butenynyl complex through alkyne dimerization instead of the expected vinylidene complex (Scheme 17, top left).[195] This complex proved to be an effective catalyst for alkyne dimerisation (Scheme 17), whereas reactions of *cis*-$[RuCl_2(dppe)_2]$ only led to the vinylidene complex. In fact, despite using 100 equivalents of alkyne, no dimerisation was observed when using dppe.[195] This difference was explained by either the smaller steric bulk of dppm facilitating coordination and reaction of a second equivalent of alkyne, or deriving from the hemilability of dppm allowing access to a vacant coordination site. In fact, a $\kappa^1$ coordinated dppm complex was tentatively identified during mechanistic studies.[195]




**Scheme 17**. Ru catalysed dimerization of alkynes

**Limitations when forming amine-borane complexes and in dehydrocoupling: strong ligand binding**

Bite angle effects in amine-borane binding were initially demonstrated with Rh(I) complexes bearing two monodentate phosphine ligands, which showed that increasing the size of the phosphine ($P^iPr_3$ vs. the smaller $P^iBu_3$) gave wider P-Rh-P bite angles, and yet X-ray crystallography revealed shorter bond distances in the Rh-H-B interaction with $H_3B{\cdot}NMe_3$.[78] This was explained with the aid of a Walsh diagram (Figure 2) with the decreasing energy of the LUMO ($b_2$, not occupied for $d^8$ Rh(I)) favouring overlap with the σ-donor $H_3B{\cdot}NMe_2$ ligand.[78] This has an effect on the catalytic dehydrocoupling of amine-boranes because the $P^iPr_3$ catalyst with a more strongly bound ligand had a lower turnover frequency. Studies with chelating diphosphines ($C_2H_4$ – $C_5H_{10}$ backbones) revealed that $[Rh(dppe)(C_6H_5F)]^+$ did not form a complex with $BH_3BMe_3$ (dppm was not investigated), and although dppe was not catalytically active, catalytic activity increased with decreasing bite angle dppp > dppb > $Ph_2PC_5H_{10}PPh_2$.[196] Recent work has demonstrated that for the smaller bite angle dcpm ligand, great care needed to be taken if amine-borane binding was to be achieved due to very favourable binding to arenes. The $[B(Ar^F)_4]$ anion was replaced with the perfluorinated $[Al\{OC(CF_3)_3\}_4]$ anion and very weakly binding $\eta^6$-tri- and di-fluoroarenes were used as the precursor. $BH_3{\cdot}NMe_3$ σ-complexes could then be synthesised, but attempted dehydrocoupling of $H_3B{\cdot}NMe_2H$ revealed slow catalysis with a bridging borylene formed in preference.[197]

## Conclusions and Outlook

Over the last two decades, small bite-angle diphosphorus ligands with single-atom linkers have shown excellent properties as ligands in homogeneous catalysis. They are now well established ligands in catalysis with often complementary properties to wide bite angle ligands such as those that are industrially important in hydroformylation and hydrocyanation reactions. The nature of the P substituents have been shown to be very important in developing successful catalysts, with very

electron-donating ligands particularly useful for hydrogenation and hydroacylation reactions that feature oxidative addition of H-H or RC(O)-H bonds respectively. Aryl substituents have been preferred in the development of ethene oligomerisation and hydrogen borrowing catalysts, whereas both alky and aryl substituents have been used in ethene polymerisation and ethene / CO copolymerisation catalysis. A general conclusion is that the most successful ligands were often the most sterically bulky examples for both diaryl and dialkyl P donors. $^{t}$Bu, *ortho*-methoxy and *ortho*-isopropylphenyl substituents often gave catalysts with the best properties including the production of longer chain polyethylene with reduced branching, or increasing the selectivity in ethylene oligomerisation catalysis. This could be due to the intrinsically reduced steric profile of diphosphorus ligands with a single-atom linker because the substituents protrude less towards the metal centre. Therefore, very bulky substituents do not completely block the coordination environment at the catalytic centre. The beneficial properties of sterically bulky substituents have been noted in other classes of ligands as well, such as α-diimine and bis(imino)pyridine ligands.[112] Very sterically bulky substituents were also successfully applied in asymmetric hydrogenation reactions and these ligands often gave excellent enantioselectivities. Overall, PCP and PNP ligands perform similar roles in the above catalytic examples, as long as ligand backbone deprotonation or reactivity is not an issue. Attention has been drawn a number of times to the hemilability associated with ligands featuring four-membered chelates, and this gives rise to the potential for large mechanistic differences when using ligands with single-atom linkers compared to dppe, dppp and other ligands. The outlook for the continued development of small bite angle ligands is very bright with a number of under-explored areas that could hold great potential in harnessing these ligands in catalysis. π-accepting small bite-angle ligands are almost completely unknown, yet could be synthesised with sterically large electron withdrawing substituents in order to exploit the Thorpe-Ingold effect and enhance chelation. There has also only been a handful of hybrid ligands explored, but this class of ligand could be important in the future, and not just for small bite angle ligands, as they offer an additional degree of electronic control over the binding sites on the catalytically active metal centres.

## Conflicts of interest

There are no conflicts to declare.

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