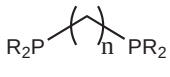
# 5 Tripodal phosphine ligands

## *5.1 Introduction*

The use of tetraphosphine ligand sets in the field of octahedral (hexacoordinate) metal complexes is well explored, particularly the use of monodentate phosphine ligands with halide, hydride and carbonyl co-ligands. However the use of monodentate phosphine ligands provides very little control of the structural properties of the complex. Bidentate phosphine ligands such as dmpe, depe, dppm, etc (Figure 5.1, **A**) induce a degree of constraint upon the metal, limiting the structural possibilities to *cis* and *trans* isomers. The geometry that is ultimately adopted is significantly affected by the nature of both the substituents and backbone of the chelating phosphine ligand.[1] Furthermore, complexes of bidentate phosphine ligands may undergo isomerisation either during further reactions or due to thermodynamic instability, which may be unfavourable in light of kinetic and mechanistic complications.[2,3] Tridentate phosphine ligands (Figure 5.1, **B**) usually do not offer any distinct advantages over bidentate ligands, as there is typically competition between *mer* and *fac* isomers.[4-7]

Tetradentate phosphine ligands are more versatile and can exist in many forms – linear (Figure 5.1, **C**), tripodal (Figure 5.1, **D**), or cyclic (Figure 5.1, **E**). Of these, only the tripodal ligand structure affords complexes having a single geometry (*cis*). Whilst literature examples of tripodal

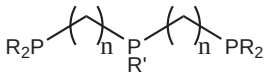
tetraphosphine ligands are typically symmetrically substituted, examples exist in which the alkyl chain length between the three 'arms' varies, for example, (2-dimethylphosphinoethyl)*bis*(3-dimethylphosphinopropyl)phosphine ($P^2P^3P'_2$) and *bis*(2-dimethylphosphinoethyl)(3-dimethylphosphinopropyl)phosphine ($P^3P^2P'_2$).[8]




R = Me, Et, Ph, etc

n = 1, 2, 3

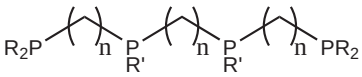
**A**




R, R' = Me, Et, Ph, etc

n = 1, 2, 3

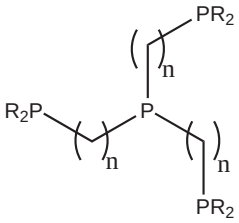
**B**




R, R' = Me, Et, Ph, etc

n = 1, 2, 3

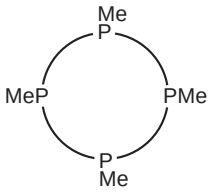
**C**




R = Me, $^i$Pr, Ph, etc

n = 2, 3

**D**



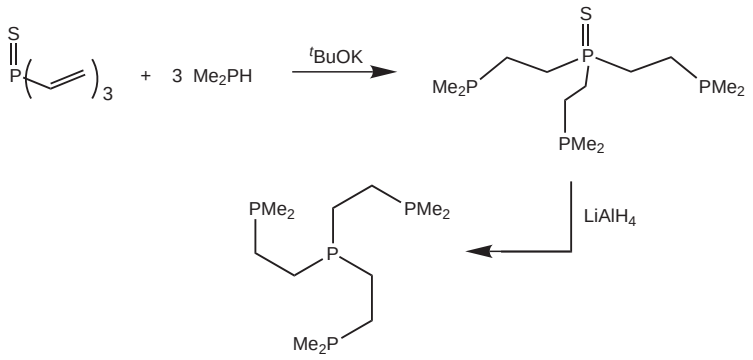

**E**

**Figure 5.1 – Types of poly-phosphine ligands**

A common system of abbreviation for symmetrical tripodal tetraphosphine ligands (Figure 5.1, **D**) is the use of $P^nP_3(R)$, where *n* represents the number of methylene units in each branch of the ligand and R identifies the two alkyl or aryl substituents on each of the terminal phosphine atoms. Due to their early discovery and literature ubiquity, $P^nP_3(R)$ ligands where R = Ph are frequently shortened to $P^nP_3$, whilst

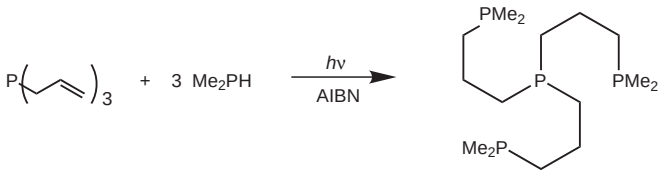
ligands of the form $P^nP_3(R)$ where R = Me may be represented as $P^nP'_3$. Thus, *tris*(2-diphenylphosphinoethyl)phosphine is abbreviated as $P^2P_3$ or $P^2P_3(Ph)$, whilst *tris*(3-dimethylphosphinopropyl)phosphine is abbreviated as $P^3P'_3$ or $P^3P_3(Me)$.

Initial development of these ligands was undertaken in the 1970s and early 1980s by King and Cloyd, who first synthesised $P^2P'_3$ *via* the base-catalysed ($^t$BuOK) addition of dimethylphosphine to trivinylphosphine sulfide, followed by reduction with $LiAlH_4$ to afford the base ligand in low yield (Scheme 5.1).[9]




**Scheme 5.1**

A significantly longer preparation involving the $^t$BuOK-catalysed addition of two equivalents of dimethylvinylphosphine sulfide to 2-(dimethylphosphino)ethyl-phosphine to provide the doubly-sulfurised tripod *bis*-(2-dimethylphosphinoethylsulfide)(2-dimethylphosphinoethyl)-phosphine, followed by reduction with $LiAlH_4$ provided a moderately improved yield of $P_2P'_3$.[9]




**Scheme 5.2**

Radiation-induced coupling of dialkylphosphine groups with trialkenephosphine bases (e.g., trivinylphosphine, triallylphosphine) has been used with some success. The propyl-chained tripodal ligand $P^3P'_3$ was first synthesised by Dahlenburg and co-workers *via* this method, with the irradiation of a mixture of dimethylphosphine and triallylphosphine producing $P^3P'_3$ in 95% yield (Scheme 5.2).[10] Photo-induced radical coupling has been extended to the preparation of the ligands $P^4P'_3$[11] and $P^2P'_3$.[12] To date, there have been no reports of tripodal poly-aryl phosphine ligands synthesised *via* photochemical methods.

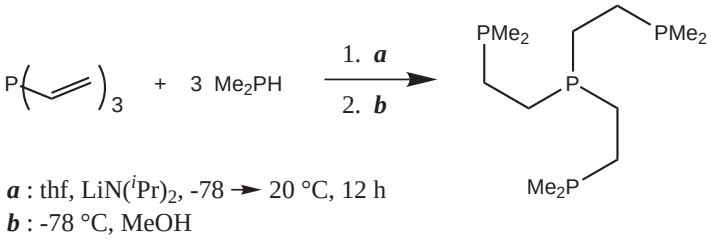
An important advancement in the synthesis of tripodal tetraphosphine ligands was the introduction of lithium diisopropylamide ($LiN(^iPr)_2$, LDA) as a catalyst in the base-catalysed coupling of trivinylphosphine and dicyclohexylphosphine to give $P^2P_3(Cy)$ in good yield.[13] Other bases such as $^t$BuOK or KOH were unable to initiate the reaction, presumably lacking the required strength to generate the $PCy_2^-$ intermediate. Lithium diisopropylamide initiates the reaction under mild (ambient) conditions and avoids possible side reactions due to its poor nucleophilicity and sterically hindered nature.

In light of these advantages, attempts to extend this method to the synthesis of the popular ligands *tris*(2-dimethylphosphinoethyl)-phosphine ($P^2P'_3$) and *tris*(2-diphenylphosphinoethyl)phosphine ($P^2P_3$), as well as the less commonly encountered propyl-bridged ligand *tris*(3-dimethylphosphinopropyl)phosphine ($P^3P'_3$), were made. Whilst the original paper[13] makes mention of preliminary studies into the synthesis of the known compound $P^2P_3(Ph)$ and the at that time unreported ligand $P^2P_3(Et)$, further details have not been forthcoming. For this reason, and partially due to the desire for a facile and economical supply of $P^2P_3(Ph)$, such studies were felt to be warranted.

## *5.2 Synthesis of tripodal phosphine ligands*

### 5.2.1 Preparation of *tris*(2-dimethylphosphinoethyl)-phosphine

T*ris*(2-dimethylphosphinoethyl)phosphine was prepared from the coupling of trivinylphosphine and dimethylphosphine which was catalysed by the addition of lithium diisopropylamide (ca. 5 mol % w.r.t. $Me_2PH$) (Scheme 5.3).




**Scheme 5.3**

The initial reaction mixture was kept cold as a safety precaution, decreasing the volatility of dimethylphosphine whilst the reagents were being introduced. The $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture after warming to ambient temperature displays signals corresponding to unreacted dimethylphosphine (−99.1 ppm), lithium dimethylphosphide (−58.4 ppm), free trivinylphosphine (−20.0 ppm), several sequential trivinylphosphine-dimethylphosphine coupling products (ca. −20 and −49 ppm), and the desired 'fully-coupled' product, $P^2P'_3$ (central phosphine −19.1 ppm, terminal phosphine −48.1 ppm). The reaction mixture was stirred at ambient temperature overnight to ensure completion of the reaction, but NMR evidence suggests a time of 2 hours would be sufficient. Methanol was added carefully at −78°C to quench residual lithium diisopropylamide and lithium dimethylphosphide. The final yield was greater than 60%, based upon the initial estimated concentration of trivinylphosphine.

Overall, the use of lithium diisopropylamide as the catalyst for the base-catalysed coupling of trivinylphosphine with dimethylphosphine offers significant improvements over alternative syntheses, producing high yields under mild reaction conditions without the need for specialised glassware or equipment. In comparison with previous syntheses there exists the advantages of not requiring irradiation (previously known to afford diphosphine side-products[3]), or extensive periods of reduction

with $LiAlH_4$ in order to remove protective sulfur groups (which is time consuming and low yielding due to incomplete reaction).[9]

Apart from the very real risks involved in the preparation and handling of dimethylphosphine, a further precaution is noted. Lithium diisopropylamide should be introduced to the reaction mixture *after* the addition of dimethylphosphine in order to avoid the direct reaction of this strong base with trivinylphosphine, which could lead to polymers and decomposition products, as occurs with triallylphosphine (Section 5.2.3).

### 5.2.2 Preparation of *tris*(2-diphenylphosphinoethyl)-phosphine

The use of lithium diisopropylamide as an alternative catalyst for carbon-phosphine bond formation in the preparation of $P^2P_3$-type tripodal phosphine ligands was also explored for the case of *tris*(2-diphenylphosphinoethyl)phosphine.

Addition of lithium diisopropylamide to a solution of diphenylphosphine and trivinylphosphine in thf at ambient temperature resulted in the formation of a deep red-coloured solution. $^{31}P\{^1H\}$ NMR spectroscopy of the reaction mixture showed complete conversion of trivinylphosphine to $P^2P_3$ after six hours, with a characteristic doublet evident at −8.2 and a quartet at −12.9 ppm attributed to the terminal and central phosphine

atoms, respectively. The remaining lithium diisopropylamide and lithium diphenylphosphide was quenched by the addition of methanol.

The overall yield was greater than 70% based upon the initial estimated concentration of trivinylphosphine. The improved yield compared to previous synthetic methods, along with the short reaction time and mild conditions required, make this method attractive for the large scale synthesis of $P^2P_3$.

### 5.2.3 Attempted preparation of *tris*(3-dimethylphosphino-propyl)phosphine

The propyl-linked tripodal phosphorus ligand *tris*(3-dimethylphosphinopropyl)phosphine ($P^3P'_3$) is typically prepared *via* the irradiation of triallylphosphine in the presence of an excess of dimethylphosphine.[10] In light of the success of employing lithium diisopropylamide in the base-catalysed coupling of trivinylphosphine with a variety of monophosphine groups (alkyl and aryl), it was hoped that lithium diisopropylamide would catalyse a similar coupling with triallylphosphine.

Addition of dimethylphosphine at −78°C to a solution of lithium diisopropylamide and triallylphosphine resulted in the formation of an orange-coloured solution. The reaction mixture was warmed to ambient temperature and stirred for 12 hours, after which time $^{31}P\{^1H\}$ NMR

spectroscopy revealed complete conversion of triallylphosphine to a species with a complicated series of resonances (Figure 5.2).

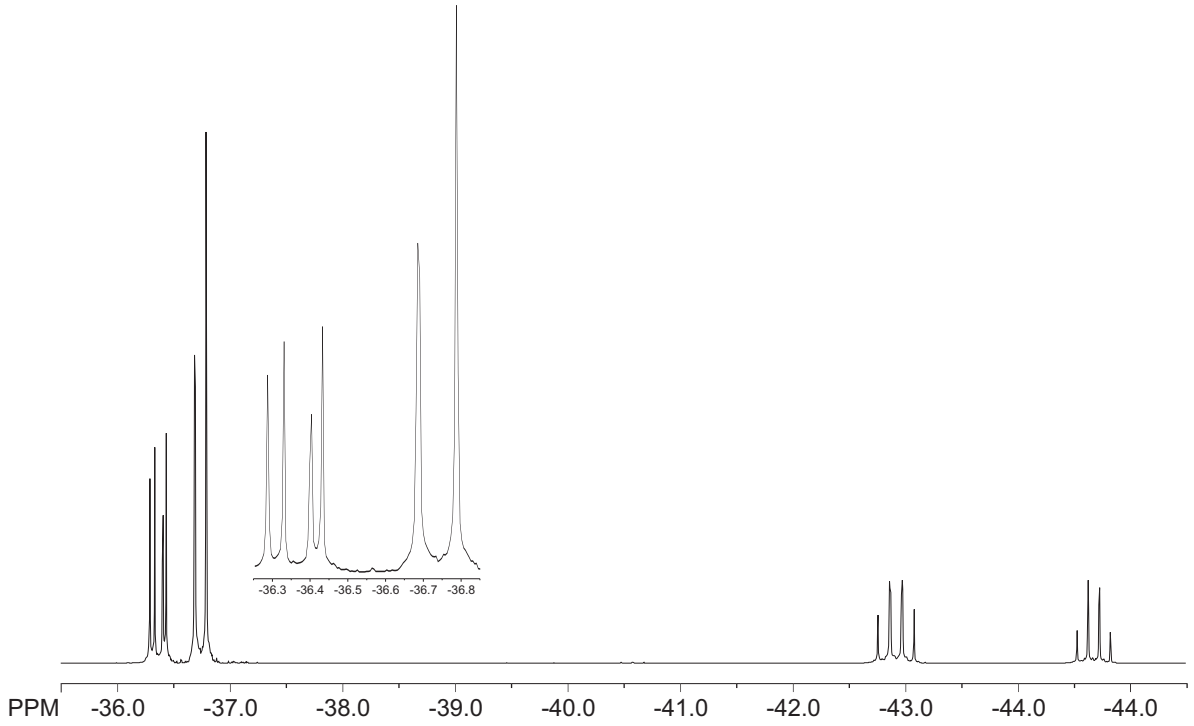



**Figure 5.2 – $^{31}P\{^{1}H\}$ NMR spectrum ($d_8$-thf/thf, 162 MHz) of the product formed from the $LiN(^{i}Pr)_2$ catalysed coupling of dimethylphosphine and triallylphosphine**

The $^{31}P\{^{1}H\}$ NMR spectrum exhibits the presence of two tripodal tetraphosphine species, with the central phosphine atom of each giving rise to the quartet resonances at $-42.9$ ($^{3}J_{(P\text{-}P)_{Av}} = 17.5$ Hz) and $-44.7$ ppm ($^{3}J_{(P\text{-}P)} = 16.0$ Hz). In the region around $-36.5$ ppm, where terminal $Me_2P$ doublet resonances are expected to occur, there exist three doublet resonances, one of which is significantly greater in intensity than the other two.

Due to symmetry requirements, tripodal tetraphosphine species give rise to $^{31}P$ NMR spectra that contain one signal from the central phosphine position, and either one intense signal from the three identical terminal phosphine positions in symmetrically substituted tripodal ligands, or one for each unique terminal phosphine position. In addition, tripodal phosphine ligands with three or more carbon units between phosphorus atoms are not expected to display P-P coupling. For example, the $^{31}P\{^{1}H\}$ NMR spectrum of *tris*(3-dimethylphosphinopropyl)phosphine consists of a singlet at $-34.4$ ppm for the central phosphine atom and a singlet at $-54.2$ ppm for the three terminal phosphine groups.[10] Likewise, the $^{31}P\{^{1}H\}$ NMR spectrum of the unsymmetrical tripodal tetraphosphine ligand (2-dimethylphosphinoethyl)*bis*(3-dimethylphosphinopropyl)-phosphine ($P^2P^3P'_2$) displays P-P coupling only across the single ethylene arm.[3]

The existence of coupling in the $^{31}P\{^{1}H\}$ NMR spectrum presented in Figure 5.2 thus strongly suggests that phosphorus addition has occurred at the β-carbon of triallylphosphine, whilst the multiple resonances corresponding to terminal phosphine positions indicate a low degree of symmetry in the molecule. Indeed, these data point towards a structure in which dimethylphosphine addition has occurred across the double bonds in triallylphosphine such that the new carbon-phosphine bond is formed non-stereoselectively at the β-position, introducing chirality to this carbon position and giving a racemic mix of stereoisomers. Due to both their symmetry and the identical NMR chemical shifts of

enantiomers in the absence of chiral resolving agents, the $^{31}P\{^{1}H\}$ NMR spectrum appears relatively simple with the resonances being assigned to the two enantiomeric pairs RRR/SSS and RRS/SSR of *tris*(2-dimethylphosphinopropyl)phosphine (*sec*-$P^3P'_3$) (Figure 5.3).

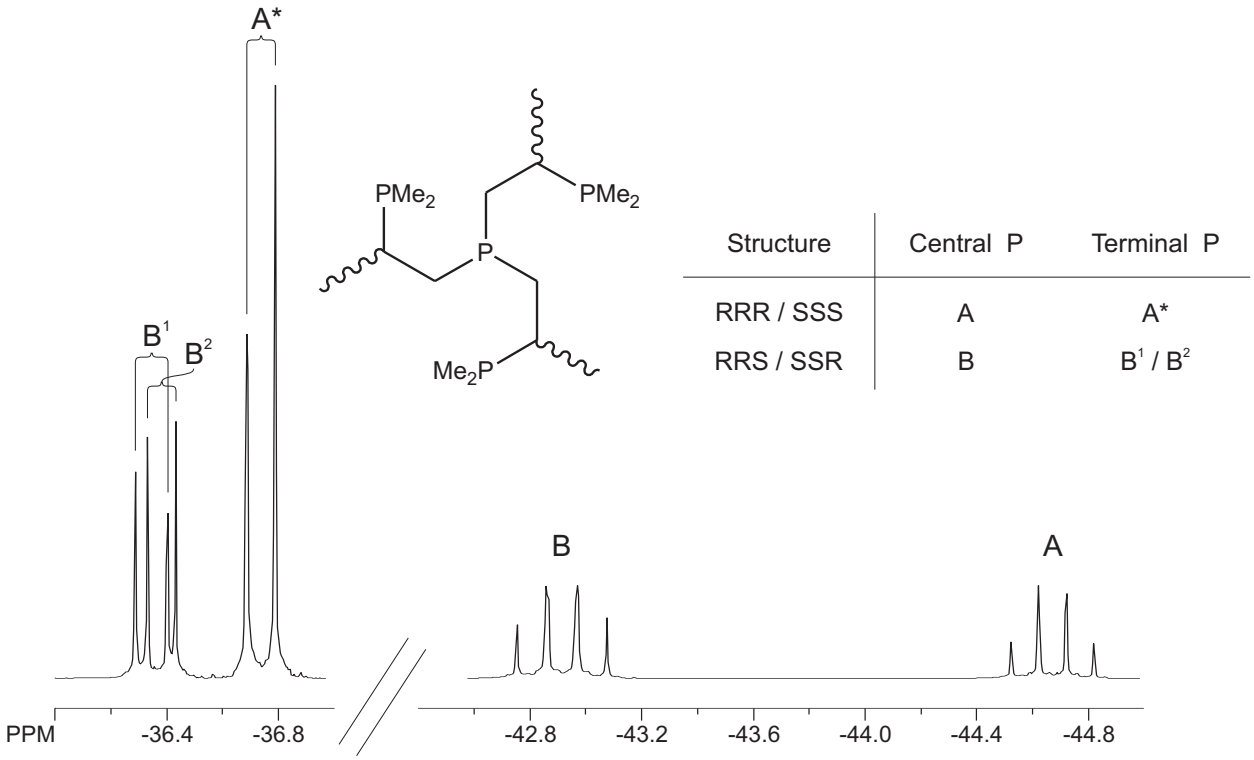



**Figure 5.3 – Assigned $^{31}P\{^{1}H\}$ NMR spectrum of *sec*-$P^3P'_3$ in $d_8$-thf**

The formation of the new carbon-phosphorus bond at the β-position occurs due to base-catalysed double-bond migration prior to the addition of dimethylphosphine across each of the three double bonds. The introduction of lithium diisopropylamide to the triallylphosphine solution prior to the addition of dimethylphosphine no doubt facilitated this process; however, dropwise addition of triallylphosphine to a solution of dimethylphosphine and lithium diisopropylamide at −78°C

resulted in the formation of the same products upon warming. Plausibly, this is because no reaction occurred until the reaction mixture warmed up and the rate of double bond migration is faster than the rate of the addition of dimethylphosphine across the double bond.

The ability of lithium diisopropylamide to catalyse the isomerisation of triallylphosphine to the $P(CH{=}CHCH_3)_3$ derivative was explored by $^{31}P\{^1H\}$ NMR spectroscopy. A solution of triallylphosphine and excess lithium diisopropylamide in $d_8$-thf was prepared and immediately frozen in liquid nitrogen. The frozen sample was then transported to the NMR spectrometer, thawed and quickly inserted into the machine. After only five minutes there was evidence of a reaction, with a new species appearing at −20.0 ppm in addition to the triallylphosphine peak at −38.2 ppm. Within one hour the triallylphosphine peak had decreased in intensity significantly, whilst the resonance at −20.0 ppm had grown. In addition, two new signals were evident at −15.3 and −18.0 ppm, the latter being the dominant peak in the spectrum. These new resonances, in order of increasing downfield shift, represent sequential double-bond migration events (structures **B** to **D** in Figure 5.4). In comparison, trivinylphosphine possesses a $^{31}P$ chemical shift of −19.8 ppm, supporting the observed downfield shift that occurs with each double-bond migration from allyl to 1-propenyl group.

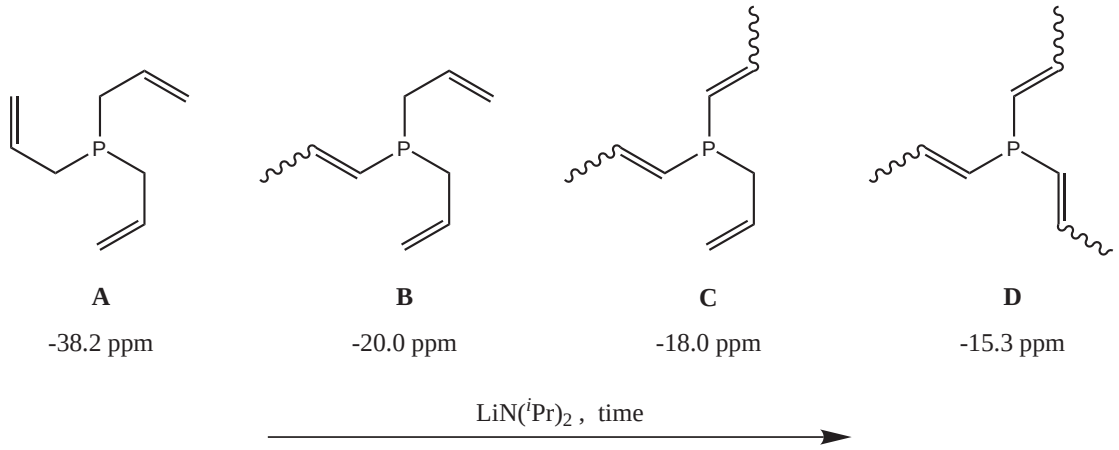



**Figure 5.4 – $LiN(^{i}Pr)_2$ catalysed sequential double-bond migration in triallylphosphine, including $^{31}P\{^{1}H\}$ NMR chemical shift values**

Extended reaction duration (5 days) led to a complex mixture of degradation products.

## *5.3 Conclusions*

The use of lithium diisopropylamide as the catalyst in the addition of a P-H bond across a carbon-carbon double bond has proved to be a significant improvement over previous synthetic methods in the preparation of symmetrical tripodal phosphine ligands with a two-carbon chain. Ligands successfully prepared by this method include the literature example $P(CH_2CH_2PCy_2)_3$,[13] and the examples reported in this chapter, $P(CH_2CH_2PMe_2)_3$ (Section 5.2.1) and $P(CH_2CH_2PPh_2)_3$ (Section 5.2.2).

However, attempted extension of this method to tripodal phosphine ligands with a three-carbon chain failed, instead giving a product where

the new carbon-phosphorus bond occurred at the β-carbon. This was ascribed to base-induced double bond migration prior to P-H addition (Section 5.2.3). Whilst the end product, $P(CH_2CH(PMe_2)CH_3)_3$ is potentially desirable, the racemic/diastereomeric nature of this compound is a drawback and the spectral complexity is significantly increased.

## References

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