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Review

Applications of ^{31}P NMR spectroscopy in development of M(Duphos)-catalyzed asymmetric synthesis of P-stereogenic phosphines (M = Pt or Pd)

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Contents

Abstract

This perspective describes the use of ^{31}P NMR spectroscopy in an ongoing research project on enantioselective P−C bond formation catalyzed by platinum and palladium Duphos complexes. This technique was used to characterize catalyst precursors, intermediates and products, to determine equilibrium and rate constants, and to measure the enantiomeric excess (ee) of the P-stereogenic phosphine products. Applications of ^{31}P NMR spectroscopy in problem-solving and identifying unexpected products, as well as the analysis of an unusual and esthetically pleasing spectrum, are also discussed.

Keywords: ^{31}P NMR; Catalysis; Platinum; Palladium; Chiral phosphines

1. Introduction

1.1. Metal-catalyzed asymmetric synthesis of P-stereogenic phosphines

Chiral phosphines are widely used ligands in metal-catalyzed asymmetric reactions [1]. They are commonly prepared by resolution or by using a stoichiometric amount of a chiral auxiliary [2]. Using a *catalytic* amount of chiral material could be more efficient [3], so we have been developing metal-catalyzed reactions for enantioselective preparation of phosphorus–carbon bonds [4]. The targets were P-stereogenic phosphines like DiPAMP (Chart 1); although its synthesis and application in asymmetric hydrogenation earned Knowles the Nobel Prize in 2001 [5], development of related ligands with chirality at the phosphorus center has been slow [6]. Instead, phosphines featuring different elements of chi-

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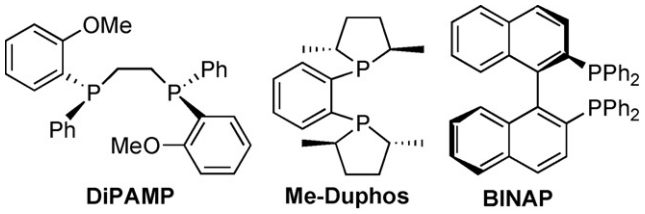


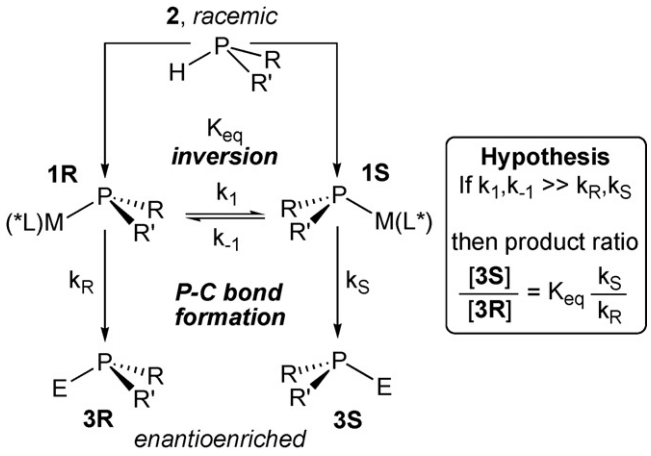
Chart 1. P-stereogenic, C-stereogenic, and axially chiral diphosphines.

rality, like BINAP and Duphos, have been more popular [7].

Phosphines (PR_3) undergo pyramidal inversion slowly [8], but inversion in metal phosphido complexes (M–PR_2) is fast, often occurring on the NMR time scale [9]. Therefore, phosphido complexes containing a chiral ligand (M(L*)(PRR')) are mixtures of rapidly interconverting diastereomers [10]. These observations suggested a general method for metal-catalyzed asymmetric synthesis of P-stereogenic phosphines (Scheme 1) [4].

The key intermediates, phosphido complexes **1**, would be formed from a catalyst precursor and the substrate, racemic secondary phosphine **2**. We hypothesized that inversion, which interconverts diastereomers **1R** and **1S**, would be much faster than their reactions with an electrophile to yield tertiary phosphines **3**, in which the substituent E comes from the electrophile. If so, P-stereogenic phosphines could be formed enantioselectively; the product ratio (enantiomeric excess) would depend on the equilibrium constant (K_{eq} = [**1S**]/[**1R**]) and the rate constants for P–C bond formation involving these diastereomers (k_S and k_R, Scheme 1) [11].

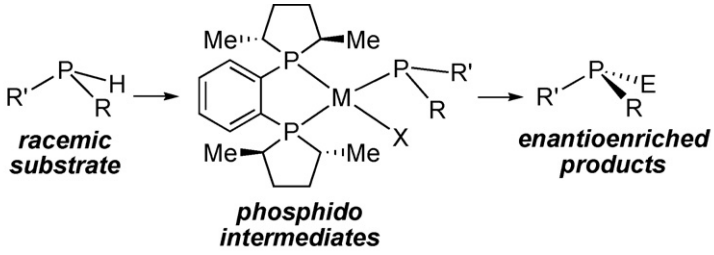
Displacement of the chiral ligand L* by the excess of phosphines present must be avoided, so we chose the rigid, preorganized chelate alkylphosphine Duphos, and developed enantioselective syntheses of P-stereogenic phosphines



Scheme 1. Metal-catalyzed asymmetric synthesis of P-stereogenic phosphines: the idea.

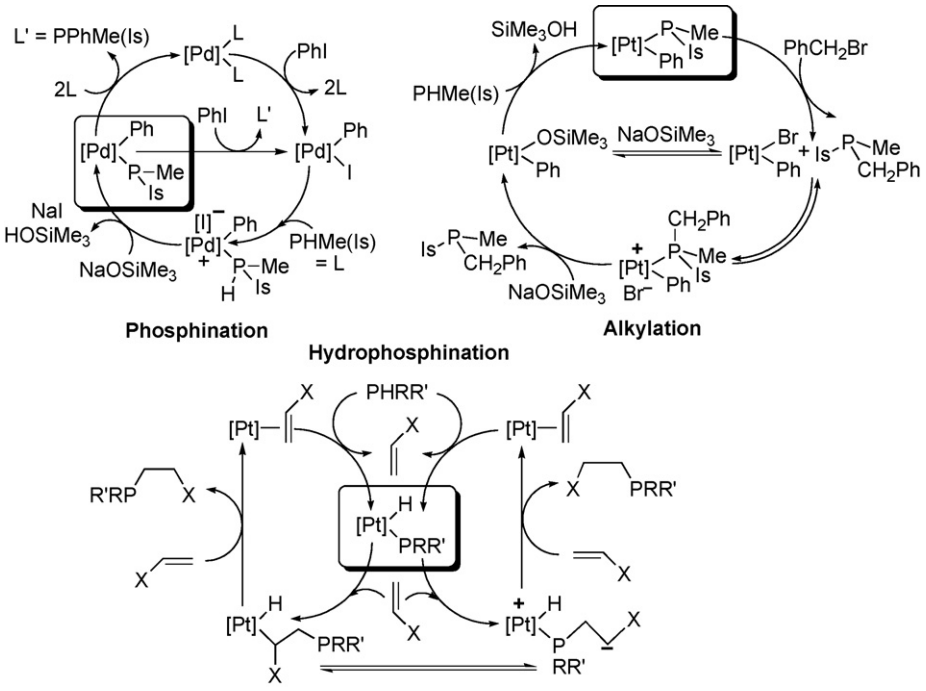
via Pt-catalyzed hydrophosphination of activated alkenes, Pd-catalyzed phosphination (cross-coupling of secondary phosphines and aryl iodides) and Pt-catalyzed asymmetric alkylation of secondary phosphines (Scheme 2) [4].

Scheme 3 shows proposed mechanisms for the reactions, with the phosphido intermediates highlighted; specific intermediates in the coupling of the secondary phosphine PHMe(Is) (Is = 2,4,6-(i-Pr)$_3$C$_6$H$_2$) with phenyl iodide or benzyl bromide are illustrated, with more generic structures in the hydrophosphination mechanism. In all cases, the interplay of P inversion and P–C bond formation as in Scheme 1 was suggested to be responsible for enantioselection. As summarized in Scheme 2, Pd phosphido complexes underwent P–C reductive elimination [12], while the phosphido ligand in analogous Pt intermediates acted as a nucleophile to attack benzyl bromide substrates [13]. The details of P–C bond formation in hydrophosphination were



M(X)	Reagents	Reaction	P-C Bond Formation
Pt(H)		Hydrophosphination (Y = CN or CO_2R)	Nucleophilic Attack or Insertion (E = CH_2CH_2Y)
Pd(Ar)	ArI base	Phosphination	Reductive Elimination (E = Ar)
Pt(Ph)	$ArCH_2Br$ base	Alkylation	Nucleophilic Attack (E = CH_2Ar)

Scheme 2. Catalytic asymmetric synthesis of P-stereogenic phosphines via M(Duphos) phosphido intermediates (M = Pt, Pd).



Scheme 3. Proposed mechanisms for M(Duphos)-catalyzed asymmetric P–C bond formation[a].
[a][M] = M(Duphos) (M = Pd or Pt), L = PHMe(Is) (Is = 2,4,6-(*i*-Pr)$_3$C$_6$H$_2$), L′ = PPhMe(Is), X = CN or CO$_2$R.

less clear and appeared to be substrate-dependent; it might occur via zwitterionic intermediates after nucleophilic attack of the Pt-phosphido group on an activated alkene, or by olefin insertion into the Pt–P bond [14].

2. Applications of ^{31}P NMR spectroscopy in M(Duphos)-catalyzed enantioselective P–C bond formation

^{31}P NMR spectroscopy is routinely used to study reactions catalyzed by metal–phosphine complexes, such as hydrogenation or hydroformylation [15]. When the substrates are phosphines, this technique becomes even more valuable for monitoring reactions and characterizing catalytic intermediates and products. This perspective describes how ^{31}P NMR spectroscopy contributed to each step of this continuing research project. It provided information on structure and bonding in diastereomeric phosphido intermediates **1** and was used to determine their barriers to pyramidal inversion, to quantify K_{eq} (Scheme 1), to measure the rate of P–C bond formation, and to assay the enantiomeric excess (ee) of the phosphine products. Finally, some examples of the use of ^{31}P NMR spectroscopy in problem-solving and identifying unexpected products, as well as the analysis of an unusual and esthetically pleasing spectrum, are also discussed.

2.1. Nature of the M–P bond in Pt- and Pd-phosphido complexes

At the beginning of this project, only one terminal phosphido complex of palladium, *trans*-Pd(PEt$_3$)$_2$(C$_6$F$_5$)(PPh$_2$), was known [16]. However, ^{31}P NMR spectroscopic data on several related platinum complexes provided useful information on structure and bonding in this functional group. In particular, the typical upfield ^{31}P NMR chemical shifts and the small $J_{Pt–P}$ coupling constants have been associated with pyramidal Pt–PR$_2$ groups and Pt–P single bonds [17]. Chart 2 shows some examples [18].

The reduced values for $J_{Pt–P}$ (and J_{PP}) in these and related complexes have been explained as a consequence of low s-character in the Pt–PR$_2$ bond, consistent with crystallographic data; the Pt-phosphido bonds were typically longer than the more common Pt–PR$_3$ bonds to tertiary phosphine ligands [17]. This analysis raised concerns about the rate of the proposed pyramidal inversion process (Scheme 1), which are summarized in Chart 3. As in organophosphines, the P hybridization in pyramidal phosphido complexes might be sp^3, or unhybridized (p^3, with an s lone pair), or somewhere in between. Pyramidal inversion via a planar transition state (sp^2-hybridized Pt–PR$_2$, with the lone pair in a P p-orbital) would then require rehybridization of the lone pair from an sp^3 hybrid or a pure s orbital in the ground

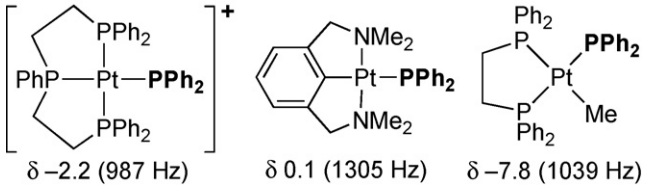


Chart 2. Selected ^{31}P NMR data (PPh$_2$ chemical shift and $^1J_{Pt–P}$) for Pt(II) diphenylphosphido complexes.

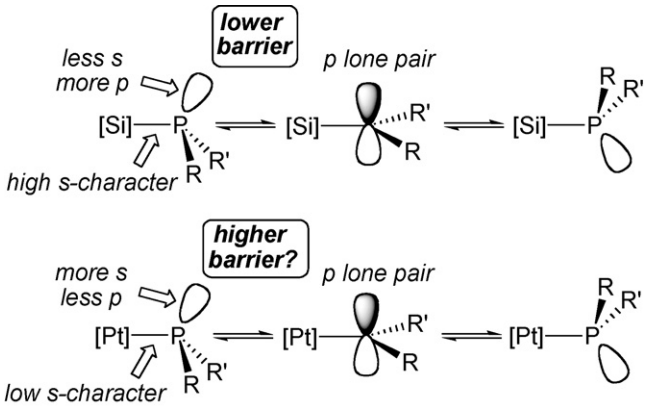


Chart 3. Effect of P substituents on the rate of pyramidal inversion via a planar transition state.

state to a p orbital in the transition state. In a related system, Mislow rationalized the reduced inversion barriers in silylphosphines: the electropositive Si substituent *increases* s-character in the P–Si bond, thus increasing the p-character of the lone pair, and decreasing the reorganization energy required to reach the transition state [19]. In contrast, the *reduced* s-character in the Pt–P bond might decrease the p-character of the lone pair, increasing the inversion barrier (Chart 3).

2.2. Fast phosphorus inversion in Pt-phosphido complexes

Despite these reservations, we found that P inversion in Pt and Pd phosphido complexes was rapid on the NMR time scale and measured barriers to this process by observing coalescence phenomena by variable temperature multinuclear NMR spectroscopy [10b,20]. Possible transition state stabilization via Pt–P p–p π-bonding was proposed [20a], but the origin of the rapid inversion remains unclear and will be addressed in ongoing computational studies.

Similar results were observed for Duphos complexes. Fig. 1 shows an example, the phosphido ^{31}P NMR signals of Pt((*R*,*R*)-Me-Duphos)(Me)(PPh(*i*-Bu)). Signals for the expected two diastereomers were observed at low temperature (bottom), but they coalesced to give the broad signal (top) on warming. The resulting approximate barrier to P inversion was 13 kcal/mol [17h].

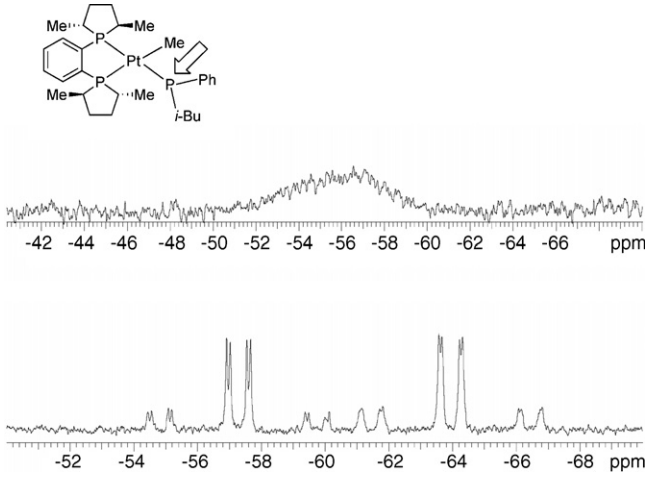


Fig. 1. Phosphido portion of the 202 MHz ^{31}P{^{1}H} NMR spectrum of Pt((*R*,*R*)-Me-Duphos)(Me)(PPh(*i*-Bu)) (toluene-d_8) at 40 °C (top) and −40 °C (bottom).

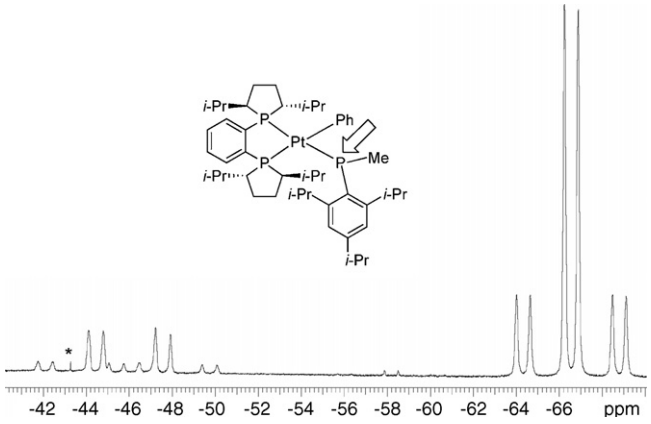
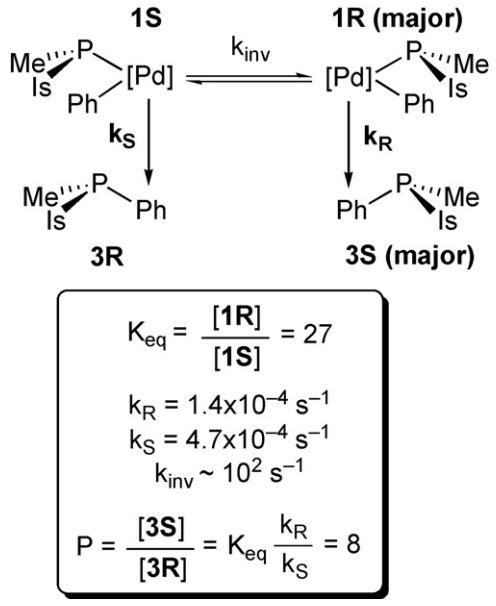


Fig. 2. Phosphido portion of the 202 MHz ^{31}P{^{1}H} NMR spectrum (THF-d_8, −50 °C) of Pt((*R*,*R*)-*i*-Pr-Duphos)(Ph)(PMeIs), showing signals due to four diastereomers. The peak marked with an asterisk is due to an impurity.

Fig. 2 shows a portion of the related low-temperature ^{31}P NMR spectrum of the analogous complex Pt((*R*,*R*)-*i*-Pr-Duphos)(Ph)(PMeIs) (Is = 2,4,6-(*i*-Pr)$_3$C$_6$H$_2$), an intermediate in Pt-catalyzed asymmetric alkylation of the secondary phosphine PHMe(Is) [13]. As desired for enantioselection (Scheme 1), the large disparity in size between the "isityl" and methyl P substituents was designed to push the equilibrium between the phosphido complexes to one side, maximizing K_{eq} (compare $K_{eq} \sim 1$ in Fig. 1, with the PPh(*i*-Bu) group). However, Fig. 2 shows an unwanted consequence of using such bulky groups, the presence of four diastereomers instead of the expected two. We assume the "extra" signals arise from conformational isomers, perhaps resulting from slow rotation about the Pt–P or P–C(Is) bonds [21].

2.3. Thermodynamics and kinetics of Pd-catalyzed asymmetric phosphination

Analogous experiments in Pd-catalyzed asymmetric phosphination provided quantitative information which was consistent with the hypothesis of Scheme 1; the same labels are used in Scheme 4 for consistency. Direct observation of the phosphido intermediates Pd((*R*,*R*)-Me-Duphos)(Ph)(PMeIs) by ^{31}P NMR spectroscopy and measurement of the temperature dependence of their equilibrium from −70 to −35 °C enabled extrapolation to catalytic conditions closer to room temperature. The rate of reductive elimination at −10 °C was determined by ^{31}P NMR spectroscopic observation of the disappearance of intermediate **1R**, the formation of enantiomeric products **3R** and **3S**, and, in the presence of PhI to trap the Pd(Duphos) fragment, the formation of Pd((*R*,*R*)-Me-Duphos)(Ph)(I). These data provided the reductive elimination rate constants in Scheme 4; note that, as hypothesized in Scheme 1, these were much smaller than the rate constants for interconversion of phosphido intermedi-



Scheme 4. Data obtained by ^{31}P NMR spectroscopy at −10 °C in THF-d_8 in Pd((*R*,*R*)-Me-Duphos)-catalyzed asymmetric cross-coupling of PHMe(Is) with PhI and in related stoichiometric reactions ([Pd] = Pd((*R*,*R*)-Me-Duphos)).

ates **1R** and **1S**, which were estimated from data for analogous Pt complexes like those in Fig. 2. Finally, the product ratio was determined after isolation of the product phosphines, again by ^{31}P NMR spectroscopy, as described below [12].

However, these kinetics results did not show if the major phosphine product came from the major or minor phosphido intermediate. This question could not be answered by ^{31}P NMR spectroscopy, but two complementary techniques provided the stereochemical results summarized in Scheme 4. The absolute configuration of an enantiomerically pure analogue of **3S**, PMeIs(*p*-MeOC$_6$H$_4$), was established by X-ray crystallography, and the configuration of the phosphido center in major intermediate **1R** was determined by ^{1}H–^{1}H NOE studies on it and the Pt analogue, along with the crystal structure of the latter [13b,21]. Assuming that P–C reductive elimination proceeds with retention of configuration at P [22] (the apparent inversion (**1R** forms **3S**) is a consequence of the CIP rules), the major enantiomer of the product phosphine was then formed from the major diastereomer of the phosphido intermediate. Thus, enantioselectivity was determined mainly by the thermodynamic preference for **1R**, although faster reductive elimination of minor diastereomer **1S** reduced the product ratio [12b].

2.4. ^{31}P NMR assay of enantiomeric excess

Every research project in asymmetric catalysis requires an operationally simple assay of enantiomeric excess [23]. When the targets are chiral phosphines, ^{31}P NMR spectroscopy of diastereomeric derivatives is a convenient method; Pd(II) reagents containing cyclometalated *N*,*N*-dimethyl(α-methylbenzyl)amines or related naphthylamines (**4** and **5**, Chart 4) are often used [24]. With monodentate phosphines (such as PMeIs(Ph) in Scheme 4) and enantiomerically pure Pd reporter complexes, two diastereomeric Pd–phosphine complexes, such as **6**, are formed by regioselective bridge-splitting of the Cl-bridged dimers **4** or **5**, which exist in solution as mixtures of *cis* and *trans* isomers [24,25]. Integration of the ^{31}P and ^{1}H NMR spectra then reveals the enantiomeric excess of the phosphine.

However, with diphosphines, both 2:1 monodentate complexes **7** and chelates **8** are possible, even with an excess of the Pd reagent [26]. Moreover, the presence of three diastereomers of the diphosphine (RR and SS = racemic plus RS = meso) leads to additional complications. For the chelate **8**, two diastereomeric complexes of the rac diphosphine are expected, as well as two diastereomeric complexes of the meso diphosphine, which differ in their regiochemistry (either the R_P or S_P end could be *cis* to the NMe$_2$ group); note that kinetic and/or thermodynamic differences between these 'meso' isomers make it likely that their ratio is not 1:1 [27]. In contrast, only three diastereomers of the bis(monodentate) complexes **7** are expected. Again, RR and SS diphosphines will form distinct complexes, and only one 'meso' complex (with inequivalent P donors) will be formed. Adding an excess of the Pd reporter complex yields only **7**, for which NMR analysis is simpler. However, spectra of **8**, even as a mixture with **7**, provide information on diastereomeric and enantiomeric excess which serves as a check on results from **7**.

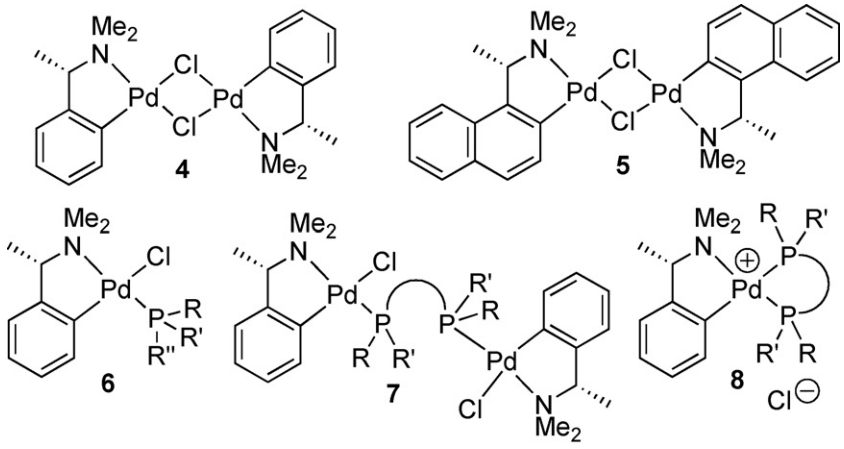


Chart 4. Commonly used Pd reagents (**4** and **5**) for assay of enantiomeric excess of chiral phosphines via formation of complex **6** (or the naphthyl analogue), and complexes **7** and **8**, which can form from C_2-symmetric chelates and **4**.

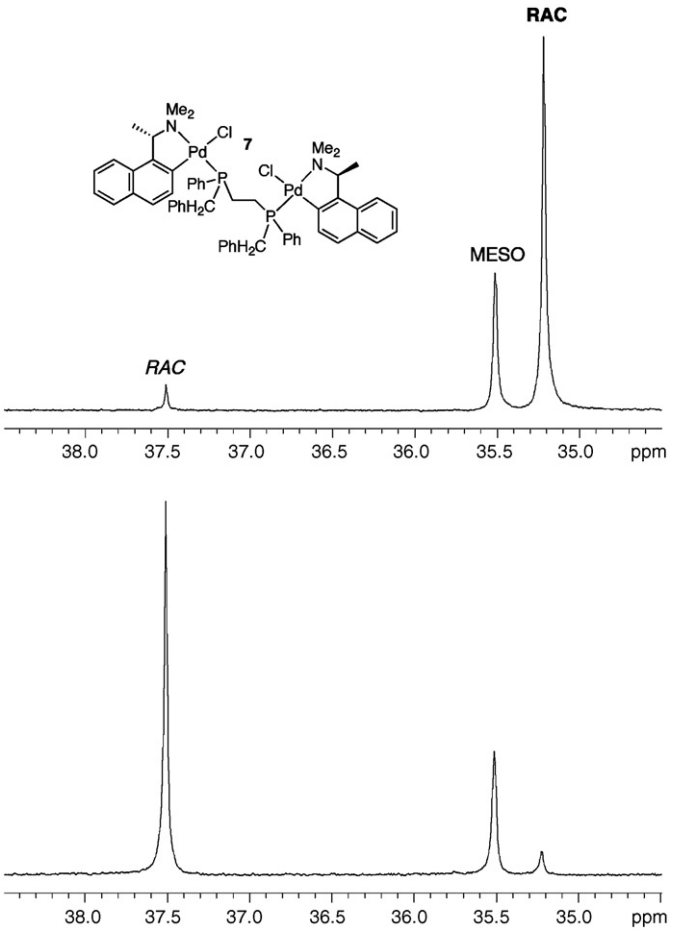


Fig. 3. 202 MHz $^{31}P\{^1H\}$ NMR spectra (CD_2Cl_2) of the complexes [Pd(*S*-$C_{10}H_6CHMeNMe_2$)(Cl)]$_2$(μ-Ph(CH_2Ph)PCH_2CH_2PPh(CH_2Ph) (**7**), containing diastereomerically and enantiomerically enriched diphosphines prepared with Pt(Duphos) catalysts of different absolute configuration. For the top spectrum, **RAC** and *RAC* indicate signals due to the major and minor diastereomers of **7** formed from the rac diphosphine, while MESO denotes signals from the analogous complex of the meso diphosphine.

With an excess of reagent **5** and the enantiomerically enriched diphosphine Ph(CH_2Ph)PCH_2CH_2PPh(CH_2Ph), prepared by Pt-catalyzed asymmetric alkylation of the bis(secondary) phosphine PhHPCH_2CH_2PHPh [13a], complexes **7** were formed. Fig. 3 shows the ^{31}P NMR spectra (CD_2Cl_2) obtained from two samples of diastereomerically and enantiomerically enriched diphosphines which were prepared with Pt(Duphos) catalysts of different absolute configurations. The dramatic variation in intensities of the peaks at 37.5 and 35.2 ppm suggests they are associated with the RR and SS diphosphines, while the δ 35.5 peak is assigned to two overlapping signals of the complex **7-meso** (with α-methylbenzylamine reporter **4**, analogous signals appeared (in C_6D_6) at δ 39.0 and 37.7 (rac) and 38.7 and 38.0 (meso)). These assignments were consistent with the rac/meso ratio of the diphosphine, measured by ^{31}P NMR spectroscopy before complexation [28].

The spectrum of Fig. 4 provided complementary information. This sample was prepared with less Pd reporter complex, so it contained a mixture of **7** and **8**. The ^{31}P nuclei in chelate **8** *trans* to N and C gave rise to well-separated doublet signals for

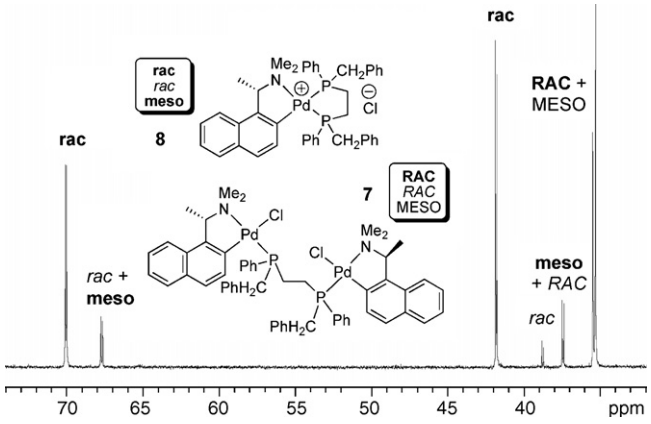


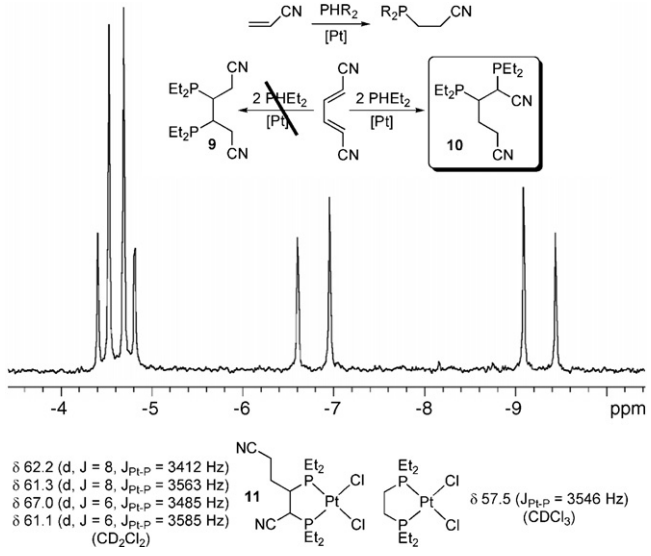
Fig. 4. 202 MHz $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2) of the complexes [Pd(*S*-$C_{10}H_6CHMeNMe_2$)(Cl)]$_2$(μ-Ph(CH_2Ph)PCH_2CH_2PPh(CH_2Ph), containing diastereomerically and enantiomerically enriched diphosphines prepared with Pt(Duphos) catalysts of different absolute configuration. In comparison to Fig. 3, this sample was prepared using less of the Pd reporter reagent, so both bis(monodentate) **7** and chelate complexes **8** were observed. Here, **rac**, *rac* and **meso** indicate signals due to the major and minor rac diastereomers and the meso isomer of **8**, while **RAC** (major), *RAC* (minor) and MESO denote signals of **7**, as in Fig. 3.

the major (**rac**) and minor (*rac*) diastereomers. Although two possible diastereomers of **meso-8** could be present, only one set of signals was observed, overlapping with peaks due to the minor isomers *rac*-**8** and *RAC*-**7**; note that the other two peaks assigned to **7** in Fig. 3 were also observed.

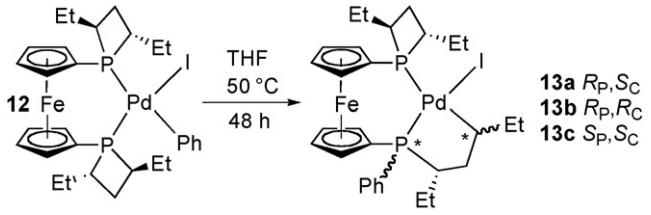
2.5. Problem-solving

2.5.1. Pt-catalyzed hydrophosphination of a diene [29]

The regiochemistry of Pt-catalyzed hydrophosphination of acrylonitrile suggested that a similar reaction of the commer-



Scheme 5. Use of ^{31}P NMR spectroscopy in determination of the regiochemistry of hydrophosphination of a diene. The spectrum (121 MHz) shows signals due to diphosphine **10** in a crude reaction mixture (C_6D_6), with data for $PtCl_2$ complex **11** and a simpler analogue given below.



Scheme 6. Phosphetane ring opening and P–C bond formation in a Pd-FerroTANE complex.

cially available diene muconononitrile would yield **9** (Scheme 5). A Pt(Duphos) catalyst might give this diphosphine in enantiomerically enriched form, as a potentially useful functionalized analogue of Chiraphos. However, ^{31}P NMR spectroscopy on crude reaction mixtures soon showed that, although a diphosphine was formed, it was not **9**, which would contain equivalent P nuclei. Instead, the observation of two AB patterns (J_{PP} = 13 and 44 Hz, respectively, Scheme 5) was consistent with the formation of two diastereomers of unsymmetrical **10**, which was later confirmed by additional spectroscopic data. For example, the chemical shifts and coupling constants in the ^{31}P NMR spectrum of the $PtCl_2$ complexes **11** were similar to those for the known complex Pt(depe)Cl_2 (depe = $Et_2PCH_2CH_2PEt_2$) [30].

2.5.2. *Pd-mediated phosphetane ring opening [31]*

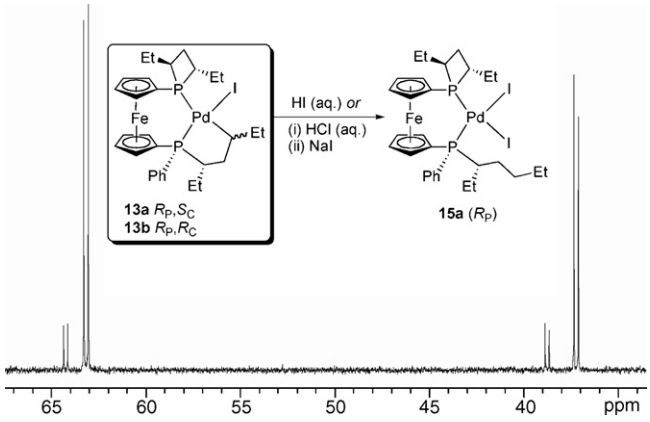
We prepared several complexes Pd(diphos*)(Ph)(I), as catalyst precursors for asymmetric phosphination, by treatment of Pd(tmeda)(Ph)(I) with a chiral diphosphine diphos* [32]. One of these, Pd((*S*,*S*)-Et-FerroTANE)(Ph)(I), which features a four-membered phosphetane ring instead of the five-membered phospholane in Duphos, decomposed in solution on standing or on mild heating to yield a mixture of complexes characterized by three pairs of doublets in the ^{31}P NMR spectrum (Scheme 6). Further investigation showed that these products resulted from opening of the phosphetane ring to yield the isomers **13**, whose J_{PP} coupling constants (48, 43, and 47 Hz) differed from those of the starting material **12** (29 Hz).

Their stereochemistry was determined by a combination of X-ray crystallography, multinuclear NMR spectroscopy including ^{1}H–^{1}H NOESY studies, and by their reactions. For example, treatment of a mixture of **13a** and **13b** with acid gave a single diastereomer of **15a** (J_{PP} = 12 Hz), which suggested that these isomers differed only in the stereochemistry at the Pd-bound carbon (Scheme 7). Diastereomer **13c** was shown to differ from **13a/13b** in its P configuration by the same reaction, which gave S_P-**15c** (J_{PP} = 15 Hz).

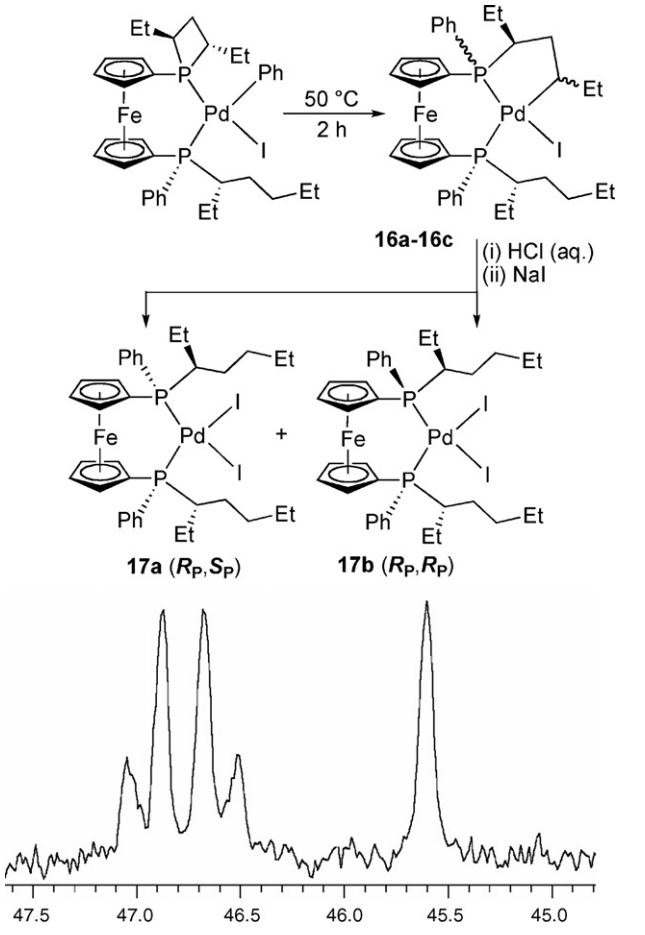
In a similar phosphetane ring opening/acid treatment sequence (Scheme 8), ^{31}P NMR spectroscopy immediately showed that a mixture of pseudo-meso **17a** and C_2-symmetric **17b** was formed – the ^{31}P NMR spectrum showed an AB pattern (J_{PP} = 21) and a singlet, respectively.

2.6. *An unusual spectrum; diastereomeric Pt-alkene complexes*

The π-complex Pt((*R*,*R*)-Me-Duphos)(*t*-butyl acrylate) (**18**) was observed as the resting state in Pt-catalyzed hydrophosphination of this alkene with secondary phosphines [14c–e]. Like analogous *trans*-stilbene complexes, it existed as a mixture of two diastereomers in which different enantiofaces of the olefin were bound to Pt [33,32]. The inequivalent ^{31}P nuclei



Scheme 7. Use of ^{31}P NMR spectroscopy in identifying the products of Pd-mediated ring opening of a complexed phosphetane. The spectrum of a mixture of **13a/13b** (202 MHz, $CDCl_3$) is shown, along with its reaction with acid to yield **15a**.



Scheme 8. A second phosphetane ring opening and 121 MHz ^{31}P NMR spectroscopic identification of the products, pseudo-meso **17a** and C_2-symmetric **17b** (mixture in CD_2Cl_2).

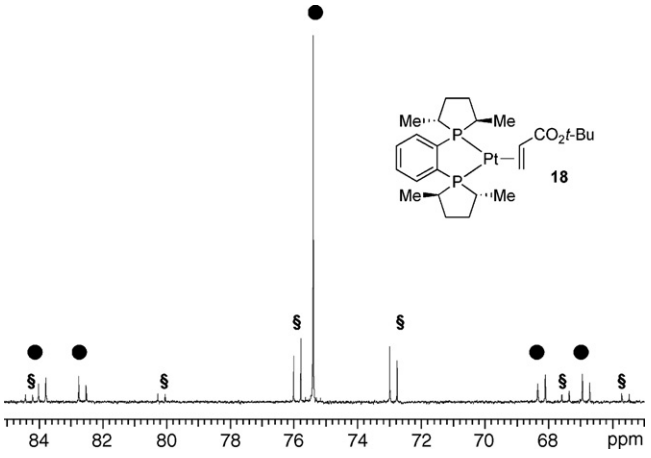


Fig. 5. 202 MHz $^{31}P\{^{1}H\}$ NMR spectrum of Pt((*R*,*R*)-Me-Duphos)(CH_2CH(CO_2t-Bu)) (**18**) in C_6D_6. The '●' and '§' symbols indicate signals due to the major and minor diastereomers, respectively.

in such complexes typically result in AX or AB ^{31}P NMR spectra, with $J_{PP} \sim 20$ Hz. Indeed, this was observed for the minor diastereomer of **18** (§ symbols, Fig. 5). Although the Pt satellite signals for the major diastereomer showed a similar pattern, instead of the expected central pair of doublets, a simple singlet was observed (● symbols, Fig. 5). This phenomenon has been observed previously; the coincidental degeneracy of the chemical shifts for the two ^{31}P nuclei ($\Delta\nu = 0$) reduces the AB spectrum to an A_2 one, where no P–P coupling is observed [34,35].

3. Conclusions

^{31}P NMR spectroscopy, a commonly used technique in studies of the chemistry of metal–phosphine complexes and their role in catalysis, becomes even more valuable for catalysis involving phosphine substrates. This perspective has provided some examples from our research on asymmetric synthesis of P-stereogenic phosphines catalyzed by Pt and Pd Duphos complexes, which continues to be guided and enriched by ^{31}P NMR spectroscopy.

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