CHAPTER

13

^{31}P NMR Spectroscopic Investigations of Low-Coordinated Multiple Bonded PN Systems

Edgar Niecke and Dietrich Gudat*

13.1. Introduction

^{31}P NMR spectroscopy is, second to x-ray crystallography, the most important and widely used analytical instrument for the characterization of structure and bonding in low-coordinate phosphorus–nitrogen compounds [1,2]. The reason for this versatility is the unique sensitivity of NMR parameters toward changes in the static or dynamic molecular structures. Several compilations of ^{31}P NMR data of low-coordinate phosphorus–nitrogen compounds published so far [3–5] provide a sufficient database for empirical comparison; however, a systematic treatment of the effects governing chemical shielding and coupling, which is of eminent importance for the elucidation of structural features from the NMR data, is available only for a very limited subset of compounds [1,5]. In this chapter, we attempt to give a systematic analysis of the influence on the ^{31}P chemical shift and coupling $^{1}J_{PN}$ in terms of substituent effects, double-bond stereochemistry, and molecular dynamics for iminophosphines and related compounds containing partial phosphorus–nitrogen triple-bond character. Although the main focus is on properties in the isotropic phase, reflecting that the majority of measurements were made in solution, the tensorial properties of the chemical shift as obtained from solid-state NMR measurements are also mentioned.

* Senior author

13.2. ^{31}P Chemical Shifts in Solution

13.2.1. General Trends

The phosphorus nuclei in compounds R–P=E–R′ containing a multiple bond to a second group V element (E=N, P, As, Sb) are among the most deshielded in the class of low-coordinated phosphorus compounds [1,6]. As compared to diphosphenes (E=P) and their heavier congeners, $\delta^{31}P$ of iminophosphines (E=N) is generally found at higher field. The difference is rather small ($\Delta\delta$ 40 ppm) in compounds containing only carbon substituents (e.g., R,R′ = C_6H_2-*t*-Bu_3 (Mes*) or *t*-Bu), which may be regarded as representatives of the unknown parent species, HP=EH, but shows a substantial increase for derivatives with more electronegative substituents (Table 13.1). As a consequence, substituent effects on $\delta^{31}P$ appear much more pronounced for iminophosphines than for diphosphenes.

Although theoretical treatment of the chemical shift in double-bond systems containing lone pairs on both adjacent atoms is extremely difficult [7], a reasonable empirical explanation of observed shifts can be given in terms of stereoelectronic influences of the substituents at phosphorus or nitrogen. In this respect, the linear correlation observed for compounds of the type R–P=N–Mes* between $\delta^{31}P$ and the lowest electronic excitation energy (Figure 13.1), which is associated with the n–π^* transition, is important [1], indicating that the relative shielding in iminophosphines is dominated by the contribution of the paramagnetic term according to the terminology of Ramsey [8].

In the following, an attempt is made to discuss the observed trends in a form that is more convenient for chemists, using a classification of substituents according to their σ- and π-donor/acceptor properties. According to a quantum chemical analysis, attachment of σ-electron-releasing (-accepting) substituents at phosphorus leads to a change of the electron distribution in the π-system, which may be described, in the language of valence bond theory, as a relative stabilization of resonance structures **1b** (**1c**), respectively (Figure 13.2). σ-Donation at nitrogen promotes a polariza-

Table 13.1. ^{31}P NMR chemical shift data for iminophosphines and diphosphenes of the type R–P=E-Mes* (Mes* = 2,4,6-*t*-$Bu_3C_6H_2$)[a]

R	Cl	*t*-BuO	Me_5C_5	*i*-Pr_2N	*t*-BuS	*t*-Bu	*t*-Bu_2P	$Me_5C_5Fe(CO)_2$
$\delta^{31}P$	135	179	195	268	314	490	570	787 (E = N)
	473	524	491	448	468	532	601	728 (E = P)
$\Delta\delta$	338	345	396	180	154	42	31	−59 —

[a] Data from ref. 1 (E = N) and 4 (E = P).

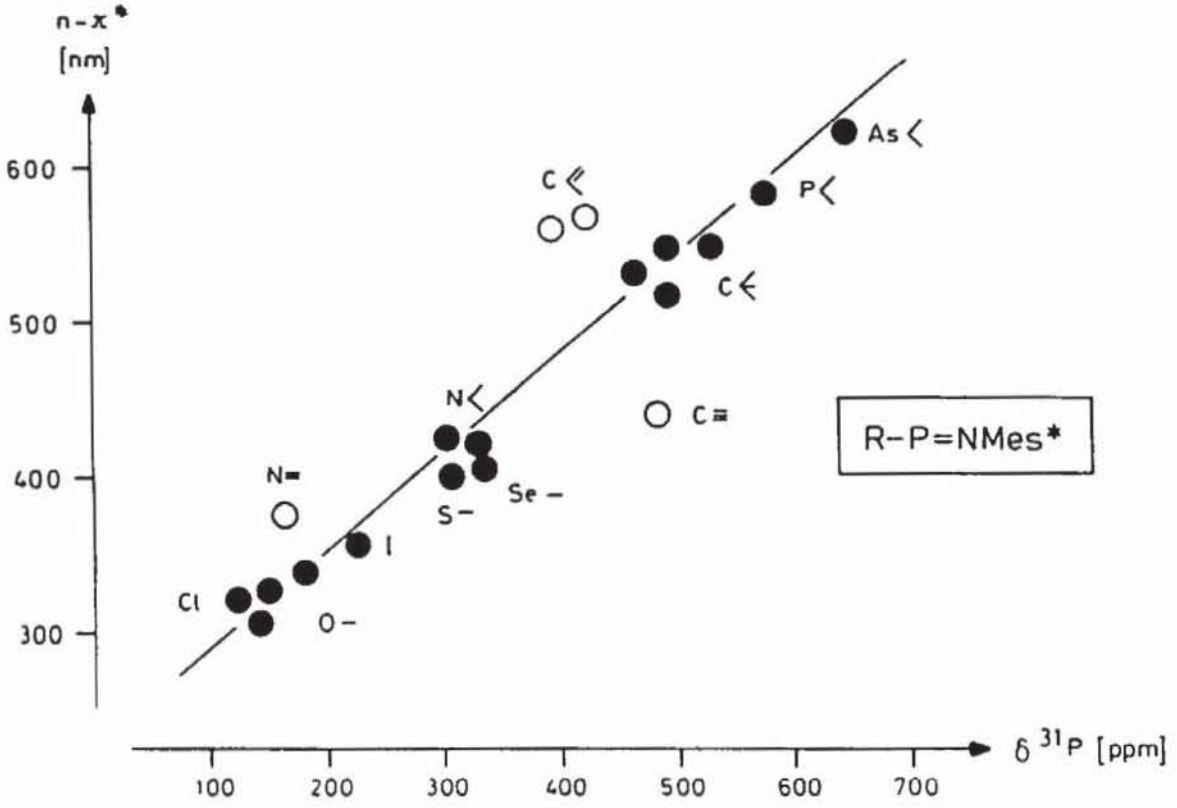

Figure 13.1. n–π^* Optical transition energies and ^{31}P NMR chemical shifts in iminophospines R-P=N-Mes* (from ref. 2).

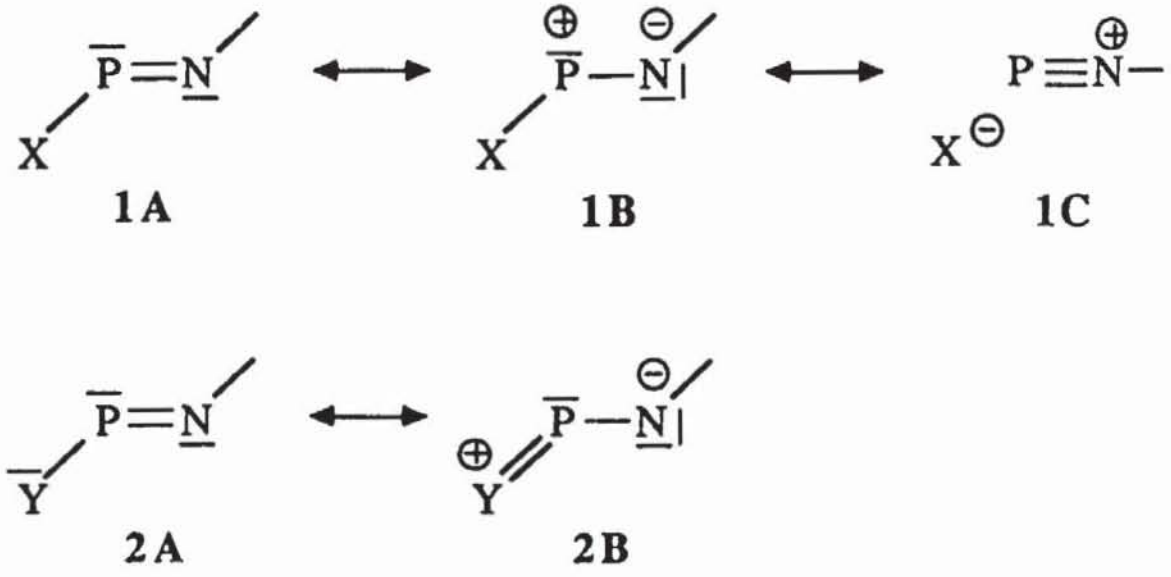

Figure 13.2. Valence bond structures of iminophosphines.

tion in the opposite direction, while π-donating groups afford a delocalization of π-electrons (**2a,b**). Taking **1a** as a reference, the phosphorus nuclei are expected to be more deshielded in **1b** and shielded in **1c** and **2a,b**.

13.2.2. Substitution Effects at Phosphorus

13.2.2.1. Carbon Substituents

The chemical shifts of iminophosphines R–P=NR′ (with R,R′ = alkyl or aryl) cover ranges between 430 and 520 ppm (R = alkyl, 14 compounds) and between 476 and 335 ppm (R = aryl, 9 compounds). The increasing inductive effect of alkyl substituents as a consequence of the replacement of β- or γ-hydrogens by methyl groups produces a systematic downfield shift (Table 13.2). The size of the shift decreases with the distance of the methyl group from the double bond and increasing degree of substitution, and it is less pronounced for variation of an alkyl group at nitrogen instead of phosphorus.

Regarding the orientation of the ligand in Mes*-P=N-*t*-Bu where the plane of the phenyl group is orthogonal to the π-electrons of the double bond [1], the higher shielding of P-arylated iminophosphines (see Tables 13.1 and 13.2) should be interpreted as a result of the lesser σ-donating capability of the sp^2 carbon rather than a mesomeric interaction. This view is corroborated by the marked upfield shift produced by introduction of electron-withdrawing CF_3 groups in the *o*-positions of a phenyl group, while the formal substitution of *o*- and *p*-hydrogens by methyls exerts the opposite effect (see Table 13.2). Conjugation of the P=N- with an adjacent olefinic double bond may be discussed for PhCH=CH-P=NMes* [11], although the observed chemical shift of 389 ppm suggests that the interaction is rather small.

An unusually large shielding is found for pentamethylcyclopentadienyl (Cp*)-substituted iminophosphines (Cp*–P=NR) whose chemical shifts are found outside the normal expectation range ($\delta^{31}P$ = 294 (R = *t*-Bu) [12],

Table 13.2. ^{31}P NMR chemical shift data for alkyl- or aryl-iminophosphines, R–P=NR′

R	Me_3C	Me_2EtC	$MeEt_2C$	Et_3C	Ref.
R′ = Me_3C	471.5	477.5	482.5	488.0	11
R′ = Et_3C	477.5	—	—	495.0	11
R	CH_3	$MeCH_2$	Me_2CH	Me_3C	—
R′ = Mes*	430	470	481	490	1,10
R	Ph	Mes	2,4,6-$(CF_3)_3$-C_6H_2		
R′ = Mes*	415	430	335		1,9,11

262 (R = NMe_2) [9], 195 (R = Mes*) [13], 138 (R = -$SiMe_3$) [13], the effect being attributed to a formal increase of the coordination number at phosphorus as a consequence of multihapto-π-bonding [13].

13.2.2.2. σ-Donating Substituents

A considerable deshielding of the phosphorus nuclei is found in phosphine- and arsine-substituted derivatives *t*-Bu_2E-P=NMes* [δ^{31}P = 570 (E=P), 640 (E=As)], and is even more pronounced in the case of compounds bearing a transition-metal substituent at phosphorus (see Table 13.1). These effects can be attributed to the strong σ-donor properties of the ligand, which should increase the weight of the polar mesomeric form (**1b**) as a consequence of either the electropositive character of the metal or of a destabilization of the lone pair at phosphorus via mutual repulsion of *n*-electrons. The effect of transition-metal substitution is substantially more pronounced than in diphosphenes, resulting in a reversal of the relative shielding between homologous compounds (see Table 13.1). A fine tuning of δ^{31}P in metalloiminophosphines $C_5R_5M(CO)_2$-P=NMes* becomes manifest in the downfield shift that is observed with increasing σ-donor strength of the metal fragment: δ^{31}P = 688 (R=H, M=Fe); 717 (R=H, M=Ru); 787 (R=Me, M=Fe [14]).

13.2.2.3. Halogen and Oxygen-Containing Substituents

The most pronounced substitution-induced upfield shift is observed for iminophosphines bearing halogens or alkoxy(aryloxy)-substituents (δ^{31}P = 218–55 ppm, 20 compounds). A rationalization of this effect is given by the combination of π-donor- and σ-acceptor properties of the substituent, which brings mesomeric structures **1c** and **2b** to the fore. The dominance of the σ-effects is suggested from the results of quantum chemical calculations and crystal structure determinations [15], which indicate a substantial increase in phosphorus–nitrogen bond order while at the same time the P–O (or halogen) bonds are weakened, according to structure **1c**. This is also in accord with the large differences of δ^{31}P between iminophosphines and diphosphenes or phosphaalkenes, respectively, in which similar mesomeric structures cannot be formulated.

The influence of the cited electronic effects on the chemical shielding is clearly demonstrated by the high-field shift of δ^{31}P that is observed in halogenoiminophosphanes with increasing electronegativity of the halogen [δ^{31}P = 218 (I), 155 (Br), 135 (Cl), 87 (F)] [1]); a similar correspondence is found for compounds RO-P=NMes* with decreasing P–O bond order [15]. A detailed analysis of the bonding was executed for the case RO = CF_3SO_2O, which exhibits the highest chemical shift of an iminophosphine known so far (δ^{31}P = 55). Both the experimental bond distances (r_{PO} 1.92 Å, r_{PN} 1.46 Å) and the results of an ab initio calculation for the model

system CF_3SO_2O-P=N-C_6H_5 suggest a description of the structure as a contact-ion pair $[CF_3SO_2O]^-$ $[P{\equiv}N\text{-}Mes^*]^+$ with a significant charge separation between the P and O atoms [q(P) 0.881, q(O) −0.836] [15].

13.2.2.4. Amino Substituents

Aminoiminophosphines RR'N-P=NR" constitute the best studied group of compounds (more than 80 derivatives are known) and are unique because both the *E*- and *Z*-configuration of the double bond is observed. The overall chemical shift range lies between 186 and 226 ppm, with *Z*-configured derivatives being more shielded (185–226 ppm, 8 compounds) as compared to the *E*-isomers (245–395 ppm).

Similar to alkoxy groups or halogens, the amino ligand simultaneously acts as a σ-acceptor and π-donor. In this case, however, the mesomeric interaction with the double-bond system (resonance structure **2b**, which is associated with a significant shortening of the P–N single bond in the crystal structures [1], is generally considered more important. Nevertheless, it should be mentioned that there is some evidence for a dominance of the σ-acceptor contribution **1c** in the *Z* form as is suggested by the characteristically long P–N single bond ($r_{P\text{-}N}$, 1.71 Å) and short double bond ($r_{P=N}$, 1.51 Å) in Ph_2N-P=NMes* [9]. Both types of substituent interactions are expected to lead to additional shielding of the ^{31}P nuclei, which is indeed observed. A separation of both effects is extremely difficult; nevertheless, the extreme high-field shift of Ph_2N-P=NMes* (195 ppm) indicates that the chemical shift experiences a stronger influence from the σ-interaction.

The influence of the double-bond stereochemistry can be assessed from the large difference of $\delta^{31}P$ observed at low temperature for *Z*-Mes*N=P-N(Mes)-*E*-P=NMes* [16] ($\delta^{31}P$ = 236 and 308). In accord with the effect of *E*/*Z*-stereoisomerism on the chemical shift of diphosphenes [6], the upfield-shifted resonance is attributed to the phosphorus in the *Z*-configured double bond. This assignment is further corroborated by the observed upfield shifts ($\Delta\delta$ 55–65) of *Z*-aminoiminophosphines with respect to corresponding *E*-derivatives bearing very similar substituents (Table 13.3).

Closely related to amino-iminophosphines are the ketimine-substituted derivatives, R_2C=N-P=NMes*. The extreme upfield shifts of these com-

Table 13.3. ^{31}P NMR chemical shift data for *E*/*Z*-iminophosphines, RR'N–P=NMes*[a]

RR'N	*E*/*Z*	$\delta^{31}P$	RR'N	*E*/*Z*	$\delta^{31}P$
i-Pr_2N	*E*	268	Mes*NH	*E*	268
Me_2N	*Z*	203	*t*-BuNH	*Z*	210
t-Bu_2C=N	*E*	179			
$C_{12}H_8C$=N	*Z*	124			

[a] Data from ref. 1 ($C_{12}H_8C$=9-fluorenylidene)

pounds (125–195 ppm) may be explained, on the basis of the results of crystal structure analyses [17], by an extremely strong π-donor interaction in which both the presence of a short P–N single bond (1.59–1.61 Å) and the almost linear arrangement of the C–P–N skeleton can be discussed in terms of a resonance structure $>C=N^{(+)}=P\text{-}N^{(-)}Mes^*$. Similar to amino-iminophosphines, a change of the double-bond stereochemistry is associated with a chemical shift difference of approximately 60 ppm (see Table 13.3).

13.2.3. Substituent Effects at Nitrogen

In contrast to the investigation of the influence of P-substitution, substituent effects at nitrogen on δ^{31}P are much less well documented. A compilation of representative examples indicates, however, that generally the same trends are observed as for P-substitution (Table 13.4), although the magnitude of the variations is significantly less pronounced. Thus, replacement of an alkyl group attached to nitrogen by a σ-electron-releasing trialkylsilyl group leads to deshielding of the phosphorus resonance, whereas the opposite effect is observed with ketimino-, silyloxy- (Table 13.4) or amino-substituents (285 ppm in *t*-Bu-P=N-NMe_2 [9]). The latter interaction is explained by the strong π-donating influence, which brings (for amino-substituents) a resonance structure of the type- $P^{(-)}\text{-}N=N^{(+)}<$ to the fore and implies an increased negative charge at the phosphorus atom. An identical explanation has been given for the upfield shift induced by π-donating substituents at the methylene carbon of phosphaalkenes [5].

13.3. ^{31}P Chemical Shifts in the Solid State

Although only isotropic chemical shifts can be measured in solution, all three principal components of the shielding tensor may be determined from high-resolution NMR spectra of solids [22]. Because changes in the molecular structure are reflected in sensitive variations of the shielding tensor, solid-state NMR spectroscopy has become an important tool for constitution analysis. Further, the comparison of the isotropic chemical shifts in the solid state (δ_{iso}) and in solution (δ_{soln}) is an indication of possible differences in molecular structure, thus allowing a judgment of the validity of a discussion of solution structures on the basis of x-ray crystal data.

Table 13.4. ^{31}P NMR shifts for iminophosphines, Mes*-P=N-R

R	*i*-Pr_3Si	Me_3Si	*t*-Bu	P-*t*-Bu_2	Mes*	N=C-*t*-Bu_2	$OSiMe_2$-*t*-Bu
δ^{31}P	500 [13]	476 [1]	452 [18]	395 [19]	395 [20]	322 [9]	315 [21]

Table 13.5. Isotropic chemical shifts δ_{iso}, δ_{soln} and anisotropy parameters $\Delta\sigma$, ρ^a for iminophosphines R-P=NMes* [23]

R		δ_{soln}	δ_{iso}	$\Delta\sigma$	ρ
Cl	Z^b	136	146	591	−0 10
Br	Z	162	141	504	−0.09
I		218	100	443	+0.62
Ph_2N	Z	198	144	362	−0.47
Carbazolyl-	Z	186	141	427	−0.45
Mes*NH	E	272	281	538	−0.87
$Ph_3Sn(t\text{-Bu})N$	E	328	346	625	−0.58
Fluorenylidene-imino-	Z	124	130	246	−0 03
$t\text{-Bu}_2C{=}N$	E	178	206	461	−0.54
Mes*N=P-N(Ad)-	Z	262	191	394	−0.81
	E		335	682	−0.72
Mes*N=P-N(*t*-Bu)-	E	272	318	554	−0.98
	E		324	657	−0 81

[a] $\Delta\sigma = \sigma_{33} - \sigma_{11}$, $\rho = (\sigma_{11} + \sigma_{33} - 2\sigma_{22})/\Delta\sigma$

[b] *E*,*Z* denote the stereochemistry as known from x-ray structures [1,9]

13.3.1. Shielding Tensors

As is generally observed for elements participating in multiple bonding, the ^{31}P nuclei in iminophosphines show a considerable chemical shift anisotropy (c.s.a.) [23,24]. Its overall magnitude seems to be smaller than for diphosphenes [25] which may be related to an upfield shift of the most deshielded tensor component, σ_{11}. Comparison of the c.s.a. data listed in Table 13.5 suggests that the multiple bond order affects the axiality parameter ρ [22], which classifies the tensor shape rather than its magnitude: a positive ρ is observed exclusively for [Mes*N≡P][$AlCl_4$] and I-PNMes*, whose crystal structure metrics [1] suggest considerable triple-bond character, whereas in all other cases ρ is clearly negative or close to zero.

Substitution effects on the shielding in amino- and alkyl-substituted iminophosphines are reflected in a significant variation of σ_{11}, whereas the smaller changes of σ_{22} and σ_{33} are of no diagnostic value [23]. If an orientation of the shift tensor relative to the molecular frame similar to that in diphosphenes [25] or phosphaalkenes [26] is assumed, σ_{11} should point approximately in the direction of the P–Y single bond in Y-P=NR. Its magnitude is then expected to be sensitive to variations of electronic transition energies within the π-electron system [25], which is indeed corroborated by the observed correlation of solution shifts and optical transition energies (see the foregoing). For the halogeno derivatives X-P=NMes* (X = Cl, Br), the higher δ_{iso} and the comparatively large tensor anisotropy result from an upfield shift of the most shielded component, σ_{33}.

A striking influence on the c.s.a. by the double-bond stereochemistry is

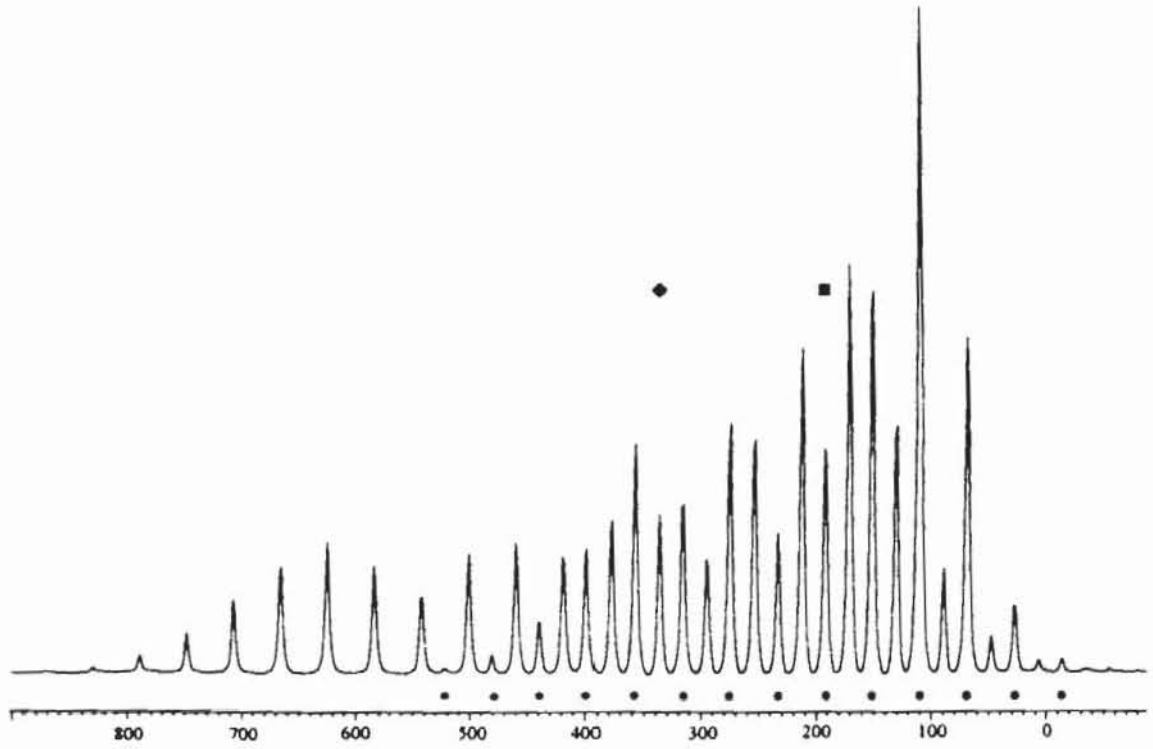

Figure 13.3. Solid-state ^{31}P MAS-NMR spectrum (161.903 MHz) of (*E*)-Mes*N=P-N(Ad)-(*Z*)-P=NMes* showing different phosphorus nuclei (δ_{iso} = 335 (♦) and 191 ppm (■)). The band system with the higher isotropic shift (*bullet*) is assigned to the ^{31}P nucleus in the *Z*-configured double bond (from ref. 23).

evident from Table 13.5, with differences of some 300 ppm being observed between *E*- and *Z*-substituted amino-iminophosphines bearing similar substituents. This effect is best demonstrated in the magic angle spinning (MAS) spectrum of (*E*-)Mes*N=P-N(Ad)-(*Z*-)P=NMes* (Figure 13.3) where the change from the *Z*- to the *E*-conformation of the double bond exclusively increases the c.s.a. by 288 ppm. In all cases, the variations of the c.s.a. are dominated by changes in σ_{11}, as for the substitution effects.

13.3.2. Isotropic Shifts

The isotropic chemical shifts of iminophosphines can show substantial differences between the solid-state and solution-phase data, which amounts to 117 ppm for I-P=NMes*. The magnitude considerably exceeds variations attributable to pure solvation effects (see the following) in several cases, thus giving evidence for differences in the molecular structures. This has been proven for I-P=NMes*, which exists in monomeric form in solution but forms dimeric species via P–I-donor/acceptor interactions in the solid state [1], relating the higher chemical shielding with a partial triple-bond order. Considering that the study of the crystal structures of different modifications of some iminophosphines [1] as well as quantum chemical calculations [27] give evidence that rather substantial "deformations" of bond angles and

even distances may easily occur, medium-dependent alterations of the molecular structure seem appropriate as a general explanation of the observed shift differences. In particular, the very low calculated nitrogen inversion barriers [27] suggest that deformation of the nitrogen valence angle is the dominating effect, which in extreme cases could even lead to different double-bond stereochemistries in the solid state and solution [e.g., the pronounced upfield shift of δ_{soln} by 58 ppm (average value) for Mes*N=P-N(*t*-Bu)-P=NMes* could be explained by a change of the double-bond conformations from (*E*,*E*) in the solid to (*E*,*Z*) in solution].

The effect of solvation on the shielding is demonstrated by the iminophosphenium salt, [Mes*N≡P][$AlCl_4$]. Although δ_{iso} of a crystalline sample containing toluene-solvated ions differed by merely −0.8 ppm from δ_{soln}, the removal of the toluene in vacuo produced a new signal with a relative upfield shift of 13.7 ppm, which was assigned to the unsolvated cation [24].

13.4. Coupling Constants

Nitrogen *J* couplings are particularly valuable in structure determination because of their sensitivity to the orientation of the lone pair and the hybridization on the nitrogen. The fast quadrupolar relaxation of the abundant ^{14}N nuclei, however, renders *J* coupling to phosphorus rarely observable because the multiplets collapse to give broadened or sharp single lines, respectively. In the case of imino-phosphines, only two exceptions from this general scheme have been reported: coupling with ^{14}N is resolved in the ^{31}P spectrum of Cp*-P=NSi-*i*-Pr_3 at elevated temperature (J = 62 Hz) [13], and the ^{31}P resonance of the cyclic zwitterion $Cl_2Ga^{(-)}$-N($SiMe_3$)-$P^{(+)}$-N($SiMe_3$) is split into a quintet by the adjacent nitrogens even at ambient temperature (J = 51 Hz). The appearance of the splitting can be related to the pseudo-cylindrical symmetry of the silyl group rather than a low n_s-electron density, as no coupling is observed for the triply bonded cation [P≡NMes*]$^+$ [1].

^{31}P–^{15}N coupling constants may be extracted either from ^{15}N satellites in the ^{31}P spectra, using Hahn-echo-extended pulse sequences or DEPT for suppression of the signals of ^{14}N-isotopomers [28], or from the ^{15}N spectra [29–31], whose sensitivity may be considerably enhanced by ^{15}N-labeling [30] or polarization transfer from ^1H or ^{31}P [28,31].

The range of known $^1J_{PN}$ coupling constants across a multiple bond is 34 to 97 Hz and covers almost the total range given by Verkade and Mosbo for tricovalent phosphorus compounds [32]. A positive sign of both values of $^1J_{PN}$ has been determined for ($Me_3Si)_2$N-P=NSiMe_3 [28]. The negative gyromagnetic ratio of ^{15}N also implies a negative reduced coupling constant, $^1K_{PN}$, as is expected for compounds with lone pairs on the coupled nuclei [33].

The magnitude of $^1J_{PN}$ corresponds to the multiple bond order. In amino

iminophosphines, $^{1}J_{PN(amino)}$ is significantly larger (76–108 Hz) than $^{1}J_{PN(imino)}$ (67–94 Hz) for each individual compound, and by far the smallest value (34 Hz) [24] is found for the triple-bonded ion $[P{\equiv}NMes^{*}]^{+}$. Assuming a positive sign of J in all cases, $^{1}K_{PN}$ becomes more positive with increasing s-character in the phosphorus–nitrogen bond, which is consistent with a greater Fermi contact contribution [33].

The comparison of $^{1}J_{PN}$ with $\delta^{31}P$ reveals that, for each type of double-bonded stereoisomer, increased ^{31}P shielding is normally associated with smaller J values (Figure 13.4a; identical stereochemistry in the solution and solid state is assumed). The dependence is significantly more pronounced in the case of the Z isomers. For the E isomers, $^{1}J_{PN}$ and $\delta^{15}N$ are similarly connected, but an inverse relation seems to hold for the Z isomers (Figure 13.4b). The observed correspondences suggest that the same factors which govern the chemical shielding in iminophosphines also have considerable influence on the coupling, even though no quantitative description has yet been attempted. Further, the observed relationships provide an additional tool for empirical assignment of the double-bond stereochemistry in favorable cases.

13.5. Dynamic Behavior

NMR spectroscopy is a valuable method, often the only one, for evaluating dynamic changes of molecular structures that may influence physical properties as well as the chemical reactivity. For iminophosphines, ^{31}P NMR spectroscopy led to the discovery of several types of dynamic processes that cause significant modifications of the multiple bonding.

13.5.1. Double-Bond Isomerization Processes

Although iminophosphines may exist as either E- or Z-isomers, normally one single configuration prevails and isomerization is not observed. An exception to this rule is constituted by certain triazadiphosphapentadienes of the formula Mes*N=P-N(R)-P=NMes* (R = Adamantyl, Mes), in which two identically substituted double bonds with different configuration occur in one molecule [16]. For the mesityl compound, their mutual interconversion can be followed by ^{31}P NMR: the two different signals observable at low temperature (−80°C) eventually collapse into a single resonance with increasing temperature because of rotations around the central phosphorus–nitrogen single bonds together with E/Z-isomerization of the double bonds [16]. The isomerization pathway cannot be determined from the NMR experiment, but quantum chemical investigations [27] suggest nitrogen inversion rather than a double-bond rotation, based on energetic considerations.

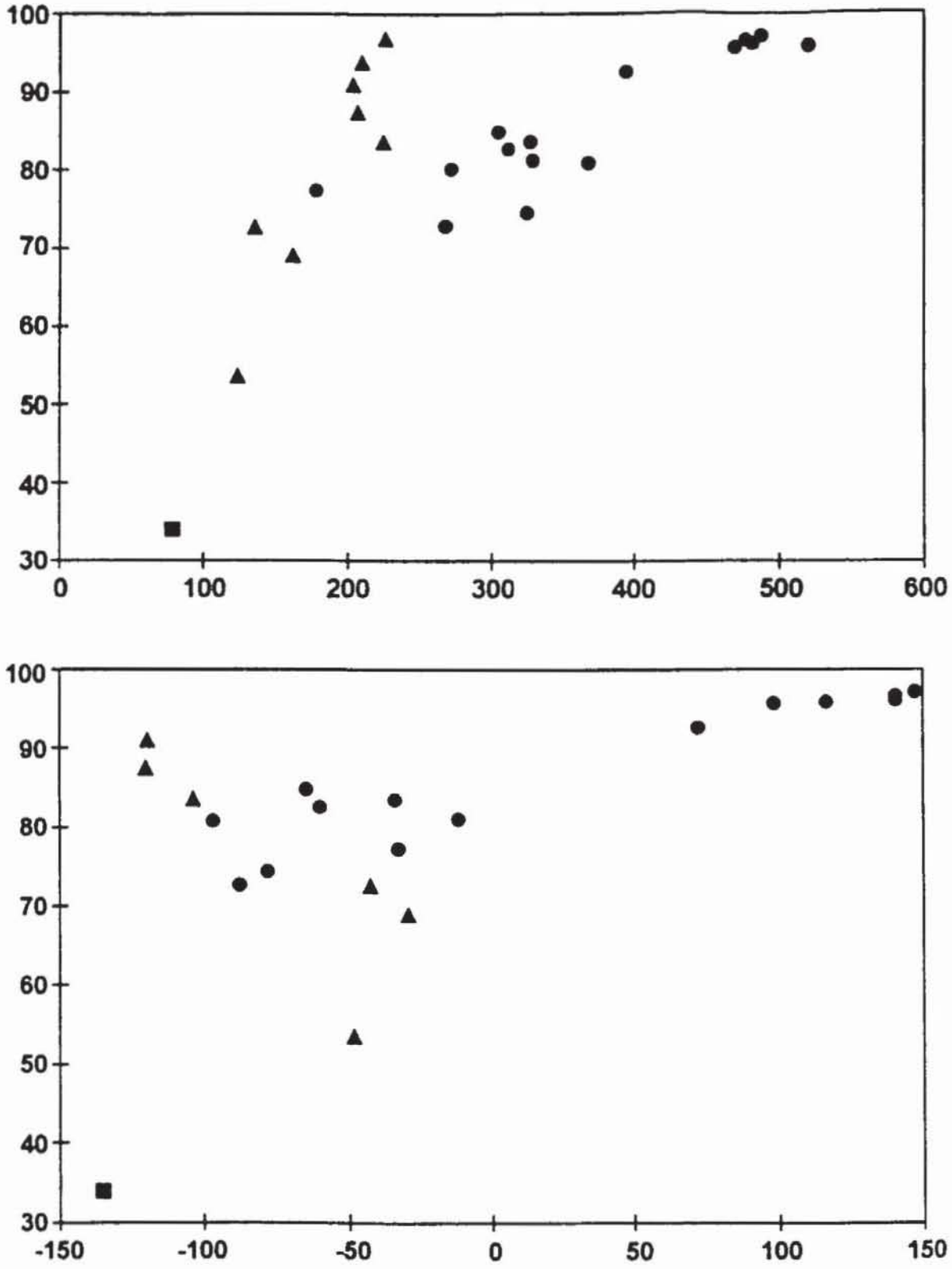

Figure 13.4. Dependence of $^{1}J_{PN}$ on $\delta^{31}P$ (top) and on $\delta^{15}N$ (bottom). Circles (triangles) denote compounds with *E*-(*Z*) configuration in solid state, respectively; square indicates the cation $[P{\equiv}NMes]^{+}$. Data from refs. 29–31.

13.5.2. Iminophosphenium-Shift Rearrangements

The analysis of dynamic changes in the ^{31}P and ^{1}H spectra of the triazadiphosphapentadienes Mes*N=P-N(Mes*)-P=NR (R = Mes*, CPh_3) proved that, in addition to the bond rotation/isomerization previously mentioned, a skeletal rearrangement involving a sigmatropic [1,3] shift of the PNR fragment takes place [16,34]. The occurrence of both processes is evident from the ^{31}P NMR spectra of a single ^{15}N-labeled sample of the derivative with R = Mes* (Figure 13.5). At −58°C, the superimposed resonances of three isotopomers with the ^{15}N label in either of the different positions of an S-shaped triazadiphosphapentadiene structure are visible, while at ambient temperature, coalescence of all resonances and concomitant averaging of all different J_{PN} couplings occurs. The dissipation of the spin label between the terminal positions is accounted for by single-bond rotations, but migration of the ^{15}N nucleus to the central position definitely

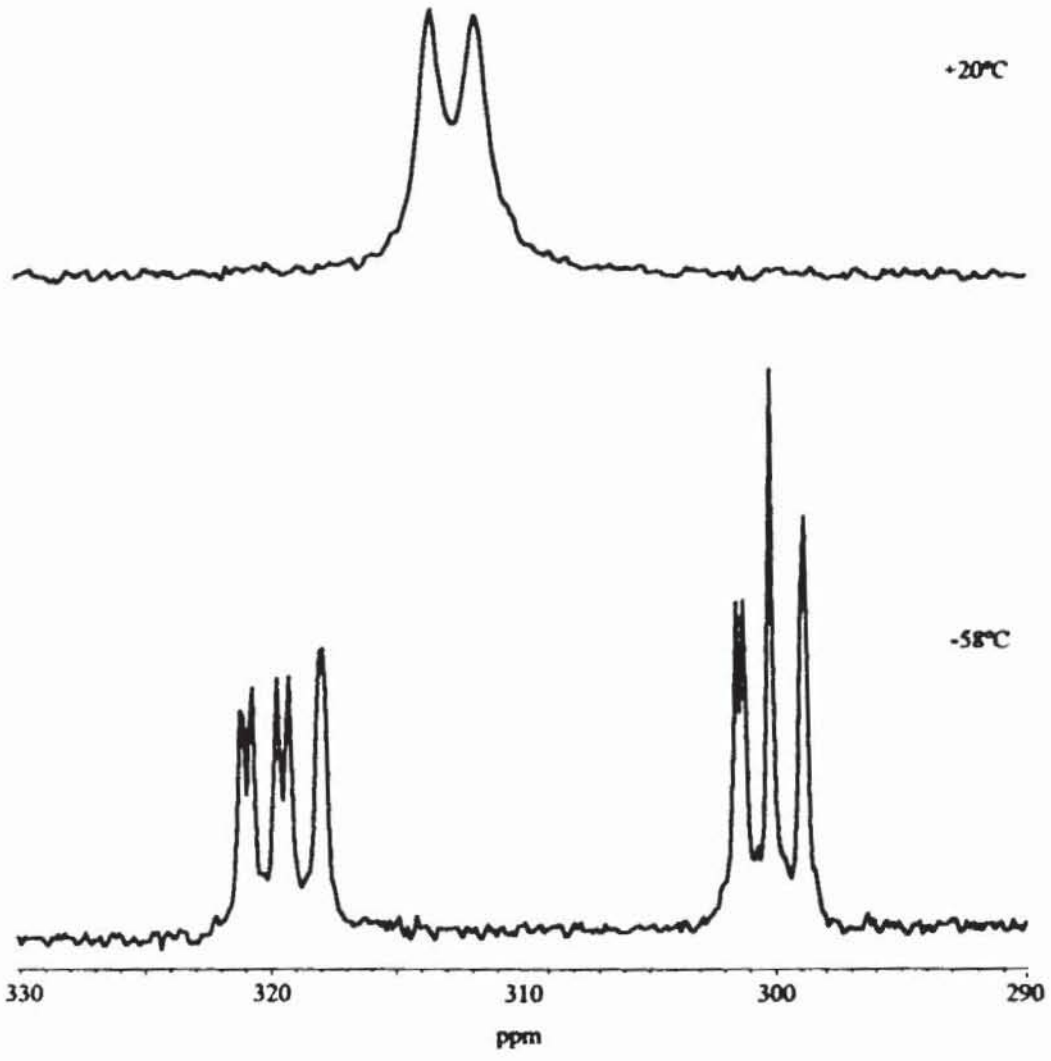

Figure 13.5. Temperature dependence of ^{31}P{^{1}H} spectrum of Mes*N=P-N(Mes*)-P=NMes*, which was labeled with ^{15}N in one position (from ref. 30).

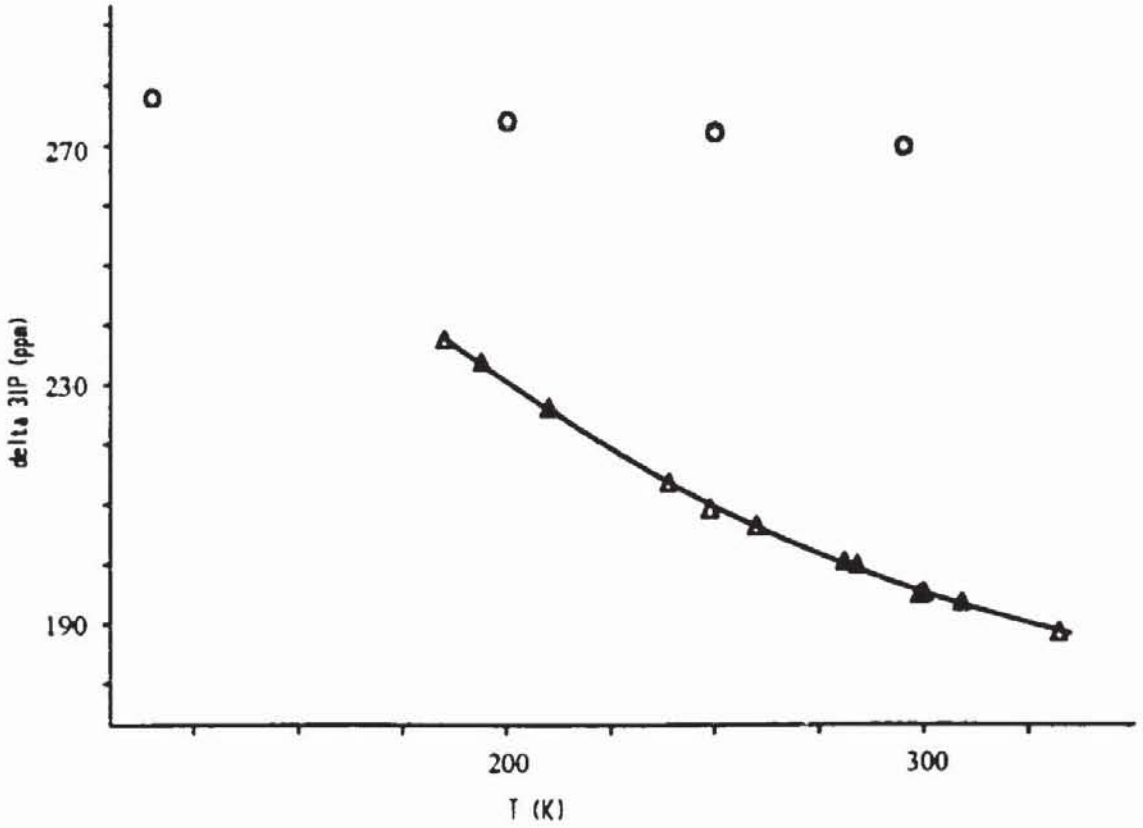

Figure 13.6. Temperature dependence of $\delta^{31}P$ in the solution (Δ) and solid state (○) for Cp*-P=Nmes*. Straight line shows results of the fit of ^{31}P chemical shift (in ppm) to the functional expression for a two-site-exchange model (T in K; from ref. 12).

requires rupture of bonds. Mechanistically, the imino-phosphenium shift is completely analogous to sigmatropic [1,3] shifts of a proton or trimethylsilyl group which were found earlier for some amino-iminophosphines [1,2].

13.5.3. Dissociation Phenomena

Partial dissociation with formation of the cation $[P{\equiv}NMes^*]^+$ and a phosphinate anion $[t\text{-}Bu_2PSe_2]^-$ was postulated to account for the unique temperature dependence of the solution ^{31}P NMR spectrum of $t\text{-}Bu_2PSe_2PNMes^*$ [1]. At −80°C, the AX pattern with chemical shifts and couplings comparable to the CP/MAS spectrum [35] suggests the presence of a contact ion pair similar to that in the solid state. The onset of dissociation into separated ions with increasing temperature leads to the disappearance of the $^2J_{PAPX}$ and $^1J_{^nSePX}$ couplings as well as a downfield shift of the resonance of the low-coordinated phosphorus nucleus [35].

13.5.4. Cyclopentadienyl Migration Processes

Pentamethylcyclopentadienyl-substituted iminophosphines Cp*-P=NR exhibit a rapid elementotropic migration [36] of the P=NR moiety around the

five-membered ring leading to signal averaging in the ^{13}C spectra both in the solution phase [12,13] and in the solid state [13]. In the case of Cp*-P=NMes*, the solution ^{31}P spectra further show a considerable upfield shift of δ^{31}P with respect to the solid and a unique temperature dependence [13] (Figure 13.6). A very similar behavior was found for the derivative with R = *t*-Bu [37]. Because all $^{13}C^{31}P$ couplings are unaffected, dissociative processes may be ruled out, and the behavior was explained by alternative pathways of ring migration, assuming a conventional [1,5]-sigmatropic rearrangement of η^1 isomers in the solid state, and a fast dynamic equilibrium between coordination isomers with η^1 or η^2 attachment of the P=NR-moiety to the ring in solution [13]. Because δ^{31}P of η^2-Cp*-coordination isomers is known to be considerably upfield shifted [38], the variation of the relative populations with temperature accounts for the observed chemical shift changes.

References

1. For a review, see Niecke, E.; Gudat, D. *Angew. Chem.* **1991**, *103*, 251; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 217, and references cited therein.
2. Niecke, E. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M.; Scherer, O J., Eds.; Georg Thieme Verlag: Stuttgart, 1990, pp 293–320, and references cited therein.
3. Cowley, A. H.; Norman, N. C. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G.; Quin, L. D., Eds.; VCH Publishers: New York, NY, 1987; pp. 621–644.
4. Lochschmidt, S.; Schmidpeter, A. *Phosphorus Sulfur* **1988**, *36*, 217.
5. Karaghiosoff, K In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M.; Scherer, O. J., Eds.; Georg Thieme Verlag: Stuttgart, 1990, pp 463–471.
6. Weber, L. *Chem. Rev.* **1992**, *92*, 1839.
7. Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR, Basic Principles and Progress, Vol. 23*; Diehl, P.; Fluck, E.; Günther, H.; Kosfeld, R.; Seelig, J., Eds.; Springer Verlag: Berlin, 1990, pp 165–262.
8. Ramsey, N. F.; *Phys. Rev.* **1950**, *78*, 695; **1952**, *86*, 243.
9. Niecke, E. (unpublished results).
10. Niecke, E.; Link, M.; Nieger, M. *Chem. Ber.* **1992**, *125*, 2635.
11. Barion, D.; Gärtner-Winkhaus, Ch.; Link, M.; Niecke, E.; Nieger, M. *Chem. Ber.* **1993**, *126*, 2187.
12. Gudat, D.; Niecke, E.; Krebs, B.; Dartmann, M. *Organometallics* **1986**, *5*, 2376.
13. Gudat, D.; Schiffner, H. M.; Nieger, M.; Stalke, D.; Blake, A. J.; Grondey, H.; Niecke, E. *J. Am. Chem. Soc.* **1992**, *114*, 8857.
14. Niecke, E.; Hein, J.; Nieger, M. *Organometallics* **1989**, *8*, 2290.

15 Niecke, E.; Detsch, R , Nieger, F ; Reichert, F., Schoeller, W. W. *Bull Soc. Chim Fr.* **1993**, *130*, 25

16 Detsch, R , Niecke, E ; Nieger, M , Reichert, F *Chem Ber* **1992**, *125*, 321.

17 Niecke, E , Gartner-Winkhaus, C , Nieger, M , Kramer, B *Chem Ber* **1990**, *123*, 477

18 Chernega, A N , Antipin, M Y ; Struchkov, Y T , Ruban, A V., Romanenko, V D *Zh Strukt Khim* **1987**, *28*, 105

19 Markovskii, L N , Romanenko, V D , Klebanskii, E O , Povolotskii, M. I , Chernega, A. N ; Antipin, M Y , Struchkov, Y T *Zh Obshch Khim* **1986**, *56*, 1721.

20 Yoshifuji, M., Shibayama, K , Toyota, K., Inamoto, N , Nagase, S *Chem. Lett.* **1985**, 237

21 Zurmuhlen, F , Regitz, M *Angew. Chem* **1987**, *99*, 65–66; *Angew. Chem Int. Ed Engl.* **1987**, *26*, 83.

22 See Herzfeld, J., Berger, A E *J Chem Phys* **1980**, *73*, 6021, and references cited therein

23 Gudat, D , Hofbauer, W ; Niecke, E (manuscript in progress), Gudat, D., Hofbauer, W , Niecke, E *^{31}P-Chemical Shift Anisotropy in $\sigma^2\lambda^2$-Iminophosphanes* Poster presentation at the XII International Conference on Phosphorus Chemistry, Toulouse, France, July 1992

24 Curtis, R D ; Schriver, M J., Wasylishen, R. E *J Am Chem. Soc* **1991**, *113*, 1493

25. Zilm, K W.; Webb, G G ; Cowley, A. H , Pakulski, M ; Orendt, A *J Am Chem. Soc.* **1988**, *110*, 2032.

26. Duchamp, J. C., Pakulski, M ; Cowley, A H ; Zilm, K. W. *J. Am. Chem Soc.* **1990**, *112*, 6803.

27. Schoeller, W. W , Busch, T ; Niecke, E ; *Chem Ber* **1990**, *123*, 1653.

28 Wrackmeyer, B ; Kupce, E ; Schmidpeter, A *Magn. Reson. Chem* **1991**, *29*, 1045.

29 Witanowski, M.; Stefaniak, L., Webb, G A In *Annual Reports on NMR Spectroscopy, Vol. 25*, Webb, G. A., Ed , Academic Press: London, 1993, 61, and references cited therein.

30. Detsch, R.; Doctoral Thesis, University of Bonn, 1992.

31 Gudat, D *Magn. Reson. Chem.* **1993**, *31*, 925.

32 Verkade, J. G.; Mosbo, J. A In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G.; Quin, L. D Eds.; VCH: New York, NY, 1987, pp 425–456.

33 Jameson, C. G In *Multinuclear NMR*; Mason, J , Ed Plenum Press: New York, 1987, pp 89–132.

34. Niecke, E.; Detsch, R.; Nieger, M. *Chem. Ber.* **1990**, *123*, 797.

35. Niecke, E.; Nieger, M.; Reichert, F.; Schoeller, W. W. *Angew. Chem.* **1988**, *100*, 1779–1780; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1713.

36. For a review on dynamics of elementotropic migrations in cyclopentadienyl compounds see Jutzi, P. *Chem. Rev.* **1986**, *86*, 983.

37. Gudat, D. (unpublished results).

38. Gudat, D.; Nieger, M.; Niecke, E. *J. Chem. Soc. Dalton Trans.* **1989**, 693.