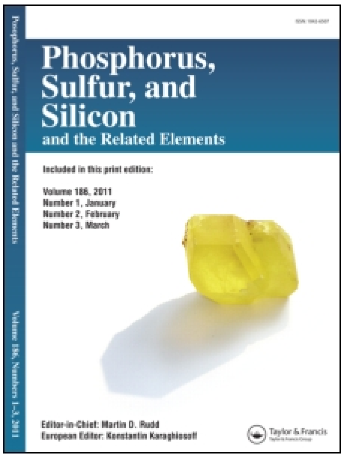


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CARBONYLMETAL COMPLEXES AND CHALCOGENIDES OF BIS(DIORGANYLPHOSPHINYL) SULFUR DIIMIDES-STUDIES BY ^{31}P NMR IN SOLUTION, USING HAHNECHO EXTENDED PULSE SEQUENCES, AND BY ^{31}P CP/MAS NMR IN THE SOLID STATE

Bernd Wrackmeyer[a]; Eriks Kupce[ab]; Stefan M. Frank[a]; Silke Gerstmann[a]; Max Herberhold[a]
[a] Laboratorium für Anorganische Chemie, Universität Bayreuth, Bayreuth, Germany [b] Institute of Organic Synthesis, Latvian Academy of Sciences, Riga, Latvia

To cite this Article Wrackmeyer, Bernd , Kupce, Eriks , Frank, Stefan M. , Gerstmann, Silke and Herberhold, Max(1992) 'CARBONYLMETAL COMPLEXES AND CHALCOGENIDES OF BIS(DIORGANYLPHOSPHINYL) SULFUR DIIMIDES-STUDIES BY ^{31}P NMR IN SOLUTION, USING HAHNECHO EXTENDED PULSE SEQUENCES, AND BY ^{31}P CP/MAS NMR IN THE SOLID STATE', Phosphorus, Sulfur, and Silicon and the Related Elements, 69: 1, 179 — 187

To link to this Article: DOI: 10.1080/10426509208036868
URL: http://dx.doi.org/10.1080/10426509208036868

Phosphorus, Sulfur, and Silicon, 1992, Vol. 69, pp. 179–187
Reprints available directly from the publisher
Photocopying permitted by license only

CARBONYLMETAL COMPLEXES AND CHALCOGENIDES OF BIS(DIORGANYLPHOSPHINYL) SULFUR DIIMIDES—STUDIES BY ^{31}P NMR IN SOLUTION, USING HAHN-ECHO EXTENDED PULSE SEQUENCES, AND BY ^{31}P CP/MAS NMR IN THE SOLID STATE

BERND WRACKMEYER,* ERIKS KUPCE,† STEFAN M. FRANK,
SILKE GERSTMANN and MAX HERBERHOLD*
Laboratorium für Anorganische Chemie, Universität Bayreuth, Postfach 101251,
W-8580 Bayreuth, Germany

(Received December 16, 1991)

For a more extensive ^{31}P NMR spectroscopic study several new sulfides of unsymmetrically substituted bis(diorganylphosphinyl) sulfur diimides, ${}^{t}Bu_2(S)P(NSN)P(S)RR^1$ ($R = R^1 = {}^{i}Pr$ (**3b**), Cy (**3c**), Ph (**3d**); $R = Ph$, $R^1 = {}^{t}Bu$ (**3e**)), were prepared. These compounds, together with the symmetrically substituted chalcogenides ${}^{t}Bu_2(E)P(NSN)P(E){}^{t}Bu_2$ (E = S (**3a**), Se (**4a**)) and carbonylmetal complexes of the type $[(CO)_5M]{}^{t}Bu_2P(NSN)PRR^1[M(CO)_5]$ ($R = R^1 = {}^{t}Bu$, M = Cr (**1a**); $R = R^1 = Ph$, M = Mo(**1b**); $R = Ph$, $R^1 = {}^{t}Bu$, M = Cr (**1c**), Mo (**1d**) and W (**1e**)) as well as ${}^{t}Bu_2\overline{P(NSN)PPh{}^{t}Bu\text{-}Mo}(CO)_4$ (**2**) were studied by ^{31}P NMR in solution and in the solid state (CP/MAS). Hahn-echo extended (HEED) pulse sequences were used to determine coupling constants $^1J(^{31}P^{15}N)$ and one-bond isotope shifts $^1\Delta^{15/14}N(^{31}P)$ for all compounds. The sign and magnitude of $^1J(^{31}P^{15}N)$ appear to be dominated by the electronic structure of the NSN system, in contrast with other P(III)-N and P(V)-N compounds. The $^1\Delta^{15/14}N(^{31}P)$ data (all negative) reflect the different types of ligands linked to phosphorus. The solid state ^{31}P NMR data correspond to the available X-Ray structures (**3a**, **4a**) and indicate, in the cases of **1d** and **3b**, that only a single isomer is present in the solid state.

Key words: Sulfur diimides; ^{31}P NMR; ^{31}P CP/MAS NMR; coupling constants $^1J(^{31}P^{15}N)$; Hahn-spin-echo; isotope shifts $^1\Delta^{15/14}N(^{31}P)$

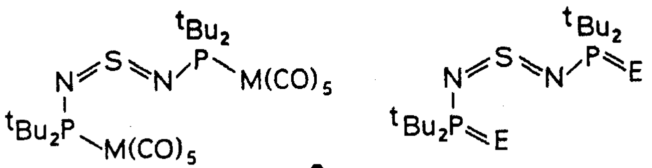
INTRODUCTION

Sulfur diimides bearing phosphinyl substituents have been used as mono- and bidentate ligands in complexes with carbonylmetal fragments.[1–3] These compounds also react readily with either sulfur or selenium to give the corresponding P(V) derivatives.[4] X-Ray analyses of some of the complexes,[1,2] a sulfide[4] and a selenide[4] have shown that the Z/E configuration **A** is preferred in the solid state, whereas ^{1}H, ^{13}C and ^{31}P NMR studies indicate that fast Z/E ⇄ E/Z rearrangement takes place in solution, even at low temperatures.[4,5] Additional NMR data, in particular those involving ^{15}N nuclei are expected to be relevant for a discussion of the bonding situation. It is also of interest to establish a relationship between the structure of

---

*Authors to whom correspondence should be addressed.

†On leave from the Institute of Organic Synthesis, Latvian Academy of Sciences, Riga, Latvia. Abbreviations: ^{i}Pr = isopropyl; ^{t}Bu = *tert*-butyl; Cy = cyclohexyl; Ph = phenyl.

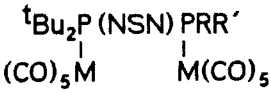


A

(M = Cr, Mo, W; E = S, Se)

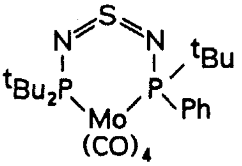
these phosphinyl sulfur diimides in solution and in the crystalline state via solid state ^{31}P NMR data.

We have therefore studied various known carbonylmetal complexes [1a,5] (**1a-e**, **2**), a sulfide[4] (**3a**), and a selenide[4] (**4a**), as well as four new sulfides (**3b-e**) by ^{31}P NMR spectroscopy. In solution, we have applied *H*ahn-*e*cho *e*xtende*d* (HEED) pulse sequences[6] in order to measure $^{1}J(^{31}P^{15}N)$ values and isotope-induced ^{31}P chemical shifts $^{1}\Delta^{15/14}N(^{31}P)$ in natural abundance. For solid state ^{31}P NMR spectra, the combination of *c*ross *p*olarization (CP) and *m*agic *a*ngle *s*pinning (MAS) has been used.

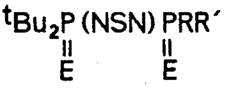


$^{t}Bu_2\underset{(CO)_5M}{P}(NSN)\underset{M(CO)_5}{P}RR'$

Nr	**1a**	**1b**	**1c**	**1d**	**1e**
M	Cr	Mo	Cr	Mo	W
R	^{t}Bu	Ph	Ph	Ph	Ph
R′	^{t}Bu	Ph	^{t}Bu	^{t}Bu	^{t}Bu



2



$^{t}Bu_2\underset{E}{\underset{\|}{P}}(NSN)\underset{E}{\underset{\|}{P}}RR'$

	3a	**3b**	**3c**	**3d**	**3e**	**4a**
E	S	S	S	S	S	Se
R	^{t}Bu	^{i}Pr	Cy	Ph	Ph	^{t}Bu
R′	^{t}Bu	^{i}Pr	Cy	Ph	^{t}Bu	^{t}Bu

RESULTS AND DISCUSSION

New Sulfides

The new sulfides **3b** to **3e** were prepared by the reaction between the corresponding unsymmetrically substituted phosphinyl sulfur diimides[7] and sulfur (see Table I for ^{1}H, ^{13}C NMR and IR data).

Hahn-Spin-Echo Experiments

^{31}P NMR spectra of solutions, recorded in the normal way, are difficult to analyse with respect to coupling constants $^{1}J(^{31}P^{15}N)$ since the integral intensity for each ^{15}N satellite amounts to just 0.18% of that for the central signal. Furthermore, the position of these weak satellite signals is unpredictably asymmetric with respect to the centre band as a result of the isotope-induced shift $^{1}\Delta^{15/14}N(^{31}P)$. However, if the intensity of the parent line can be reduced while the intensity of the ^{15}N satellites remains almost unaffected, assignment of ^{15}N satellites becomes possible. In all compounds **1** to **4a**, the sensitivity of ^{31}P NMR can be considerably enhanced using

TABLE I

Spectroscopic data of the sulfur diimides ${}^tBu_2P(S)(NSN)P(S)RR^1$ (**3b–3e**)

Compound		**3b** (R=R'=^{i}Pr)	**3c** (R=R'=Cy)	**3d** (R=R'=Ph)	**3e** (R=Ph; R'=^{t}Bu)
^{1}H-NMR: a)					
δ(^{t}**Bu$_2$P**)		1.33 d |16.8|	1.35 d |16.3|	1.09 d |16.8|	1.23 d |18.2|
					1.31 d |16.9|
δ(^{t}**BuP**)					0.96 d |16.7|
δ(R)		2.34 m	1.90 m	7.45 m	7.47 m
		1.18 d |7.0| b)		7.91 m	7.86 m
		1.23 d |7.0| c)			
^{13}C-NMR: d)					
δ((**Me$_3$**C)$_2$P)		27.1 d |1.5|	27.2 d |1.7|	26.7 d |1.5|	26.7 d |1.5|
					27.0 d |1.6|
δ(**Me$_3$**CP)					24.3 d |1.6|
δ((Me$_3$**C**)$_2$P)		40.3 d |53.4|	40.3 d |53.3|	39.9 d |52.3|	37.9 d |59.4|
					40.4 d |59.0|
δ(Me$_3$**C**P)					37.1 d |69.0|
δ(R)	**C^1**	30.8 d |62.1|	40.4 d |61.4|	134.3 d |103.9|	129.9 d |82.9|
	C^2	16.3 d |3.8|	25.7 d |2.0|	131.0 d |11.4|	128.2 d |12.2|
	C^3	16.0 d |1.0|	25.8 d |2.0|	128.6 d |13.6|	132.4 d |10.1|
	C^4		25.9 d |4.4|	131.8 d |2.7|	131.7 d |3.2|
	C^5		26.2 d |4.9|		
	C^6		26.4 d |3.6|		
IR: e)					
ν_{as}(NSN)		1179 vs	1168 vs	1166 vs	1161 vs
ν_s (NSN)		1018 m	1002 m	1018 m	1019 m

a) δ(ppm), CDCl$_3$, 27±1°C, values in | | $^3J(^{31}P^1H)$ (Hz).

b) $^3J(^1H^1H)$ = 2.6 Hz.

c) $^3J(^1H^1H)$ = 3.8 Hz.

d) δ(ppm), CDCl$_3$, 27±1°C, values in | | $^nJ(^{31}P^{13}C)$ (Hz).

e) (cm^{-1}), KBr.

*p*olarization *t*ransfer (PT) techniques,[8,9] at least for the phosphorus atoms with ^{t}Bu substituents.

The extension of the basic PT pulse sequences (INEPT,[8] DEPT[9]) by a Hahn-spin-echo pulse train (HEED pulse sequences[6]) causes a decrease in the magnetization due to the ^{31}P-^{14}N isotopomer; the parent line is slightly broadened by partially relaxed scalar coupling $^1J(^{31}P^{14}N)$. This arises from scalar relaxation of the second kind, whereas the magnetization due to the ^{31}P-^{15}N isotopomer (^{15}N satellites) decreases at a much slower rate. Indeed, if an appropriate delay (depending on the natural line width of the parent signal[6]) in the Hahn-spin-echo is selected, sufficient attenuation of the central line is readily achieved. In principle this method can be applied without initial polarization transfer. However, this requires much more spectrometer time because the recycle delay of the pulse sequence is then governed by the longitudinal relaxation rate of ^{31}P (i.e., $5 \cdot T_1(^{31}P)$). In the case of fairly diluted solutions which had to be used for most of the compounds **1** to **4a**, PT previous to the Hahn-spin-echo turned out to be essential. Representative examples of the application of HEED experiments are given in Figures 1 and 2 for compounds **3b** and **4a**, respectively. This technique facilitates the measurement of small ^{31}P-X couplings and allows to measure homonuclear ^{31}P-^{31}P couplings which are difficult to determine by other techniques. This is shown in the case of **4a** (Figure 2) where the degeneracy of the ^{31}P nuclei is removed in the satellite spectrum of the $^{31}P^{15}NS^{14}N^{31}P$ fragment. It should be noted that this coupling constant $^4J(^{31}P^{31}P)$ could not be resolved in the ^{77}Se satellite spectrum. Although the equivalence of the ^{31}P nuclei is also destroyed in the

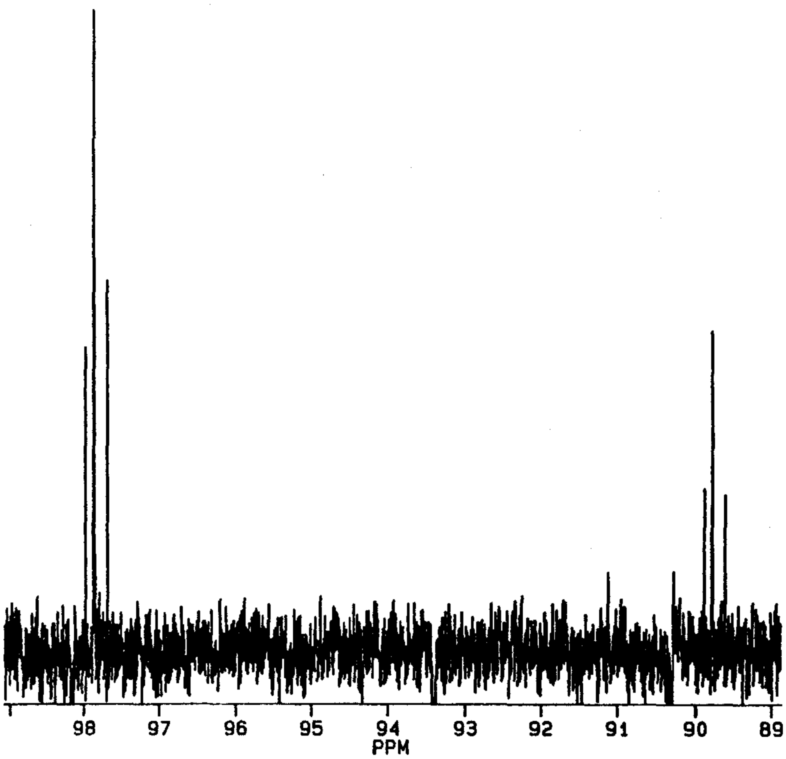


FIGURE 1 121.5 MHz ^{31}P NMR spectra (DEPT-HEED, ^1H decoupled) of $^tBu_2P(S)(NSN)P(S)^iPr_2$ (**3b**) at 27 ± 1°C in $CDCl_3$. A delay of 0.25 s in the Hahn-echo part of the sequence left the residual signal of the ^{31}P—^{14}N isotopomers, asymmetrically displaced with respect to ^{15}N satellites of the ^{31}P—^{15}N isotopomers. The deviation from 1:1 intensity of the ^{31}P NMR signals is due to different efficiency of polarization transfer.

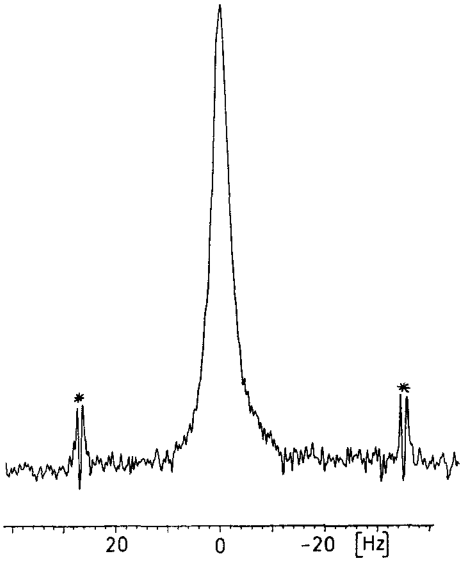


FIGURE 2 121.5 MHz ^{31}P NMR spectrum (DEPT-HEED, ^{1}H decoupled) of ^{t}Bu$_2$P(Se)(NSN)P(Se)^{t}Bu$_2$ (**4a**) at 27 ± 1°C in CDCl$_3$ (Hahn-echo delay: 0.3 s). The ^{15}N satellite signals (marked by asterisks) are split by homonuclear coupling $^{4}J(^{31}P^{31}P)$ = 1.2 Hz.

^{77}Se^{31}P^{14}NS^{14}N^{31}P(Se) fragment, the ^{77}Se satellite signals are broad like the parent line.

A further advantage of HEED experiments is the possibility to measure one-bond isotope shifts $^{1}\Delta^{15/14}N(^{31}P)$. Previously, it was necessary to prepare ^{15}N-labeled compounds in order to measure these parameters. It appears that $^{1}\Delta^{15/14}N(^{31}P)$ values may now become valuable additional parameters in NMR studies of phosphorus-nitrogen compounds.[6,10] Relevant data for coupling constants $^{1}J(^{31}P^{15}N)$ and one-bond isotope shifts $^{1}\Delta^{15/14}N(^{31}P)$ of compounds **1** to **4a** are given in Table II.

Solid State ^{31}P CP/MAS NMR Spectra

Five representative compounds (**1d**, **2**, **3a**, **3b**, **4a**) were studied by solid state ^{31}P CP/MAS NMR and the results are given in Table II. Although ^{31}P nuclei are "undiluted" spins, ^{31}P-^{31}P dipolar interactions appear to be weak and are completely averaged by MAS. Some broadening and splitting of the centre bands and spinning side bands can be traced to scalar and dipolar ^{31}P-^{14}N interactions.[11] For the compounds with known structure (**3a**, **4a**),[4] the appearance of two ^{31}P resonances (see Figure 3) is in agreement with a single type of molecule in the unit cell and two different environments (Z and E) for the phosphorus atoms. In the case of **3b**, the presence of isomers is possible. However, the ^{31}P CP/MAS spectrum showed only two resonance signals with δ^{31}P in close agreement with the solution data. The shape of the ^{31}P signals in the solid state is rather similar to those of **3a**, indicating that **3b** adopts a Z/E configuration. The same is true for the complex **1d** which also prefers a single configuration, most likely Z/E, in the solid state. Finally, the

TABLE II

Chemical shifts $\delta^{31}P$, coupling constants $^{1}J(^{31}P^{15}N)$ and one-bond isotope shifts $^{1}\Delta^{15/14}N(^{31}P)$ of compounds **1** to **4a** (in $CDCl_3$)

Compound Nr.	M,E	R	R′	$\delta^{31}P$ a) (solution)	$\delta^{31}P$ a) (solid state)	$^{1}J(^{31}P^{15}N)$ |Hz|	$^{1}\Delta^{15/14}N(^{31}P)$ |ppb| b)
1a	Cr	^{t}Bu	^{t}Bu	154.7		63.0 c)	-42.4 c)
1b	Mo	Ph	Ph	131.8 ($P^{t}Bu_2$)		52.8 c)	-51.3 c)
				87.7		not observed	
1c	Cr	Ph	^{t}Bu	150.9 ($P^{t}Bu_2$)		59.0	-48.0
				132.6		65.0	-49.0
1d	Mo	Ph	^{t}Bu	132.7 ($P^{t}Bu_2$)	134.0	58.1	-55.0
				112.8	115.0	64.8	-46.0 d)
1e	W	Ph	^{t}Bu	115.5 ($P^{t}Bu_2$)		54.3	-42.0
				94.2		63.4	-43.0
2	Mo	Ph	^{t}Bu	108.7 e) ($P^{t}Bu_2$)	105.5	53.2	f)
				80.0 e)	79.7	50.4	f)
3a	S	^{t}Bu	^{t}Bu	97.1	100.4, 94.0	60.1	-34.0
3b	S	^{i}Pr	^{i}Pr	96.4 ($P^{t}Bu_2$)	95.8	59.0	-33.1
				88.5	89.6	59.0	-34.7
3c	S	Cy	Cy	97.6 ($P^{t}Bu_2$)		59.2	-30.2
				81.7		not observed	
3d	S	Ph	Ph	98.2 ($P^{t}Bu_2$)		58.6	-38.0
				50.7		not observed	
3e	S	Ph	^{t}Bu	98.0 ($P^{t}Bu_2$)		59.0	-34.1
				76.1		59.0	-34.7
4a	Se	^{t}Bu	^{t}Bu	96.8	99.8, 94.3	61.8	-33.0

a) ^{31}P NMR spectra measured at -10°C for compounds **1**, **2**, **3b**; all other data for 27±1°C.

b) Negative sign denotes shift to lower frequency with respect to the ^{31}P-^{14}N isotopomer; ± 1 ppb if not mentioned otherwise.

c) Ref. 5.

d) ± 10 ppb.

e) $^{2}J(^{31}P^{31}P) = 33.7$ Hz.

f) The HEED spectrum gave the ^{15}N satellites out of phase which did not allow to calculate sufficiently accurate isotope shifts.

^{31}P CP/MAS NMR of **2** shows the expected two ^{31}P NMR signals with similar isotropic $\delta^{31}P$ values as in solution.

Coupling Constants $^{1}J(^{31}P^{15}N)$

A positive sign of $^{1}J(^{31}P^{15}N)$ [reduced coupling constant $^{1}K(^{31}P^{15}N) < 0$; $^{1}K(AX) = {}^{1}J(AX)\cdot 4\pi^{2}(\gamma_A\cdot\gamma_B\cdot h)^{-1}$] can be safely assumed for P(III)—N compounds,[12] including phosphinyl sulfur diimides, the precursors of **1** to **4a**. In $^{t}Bu_2P(NSN)P^{t}Bu_2$

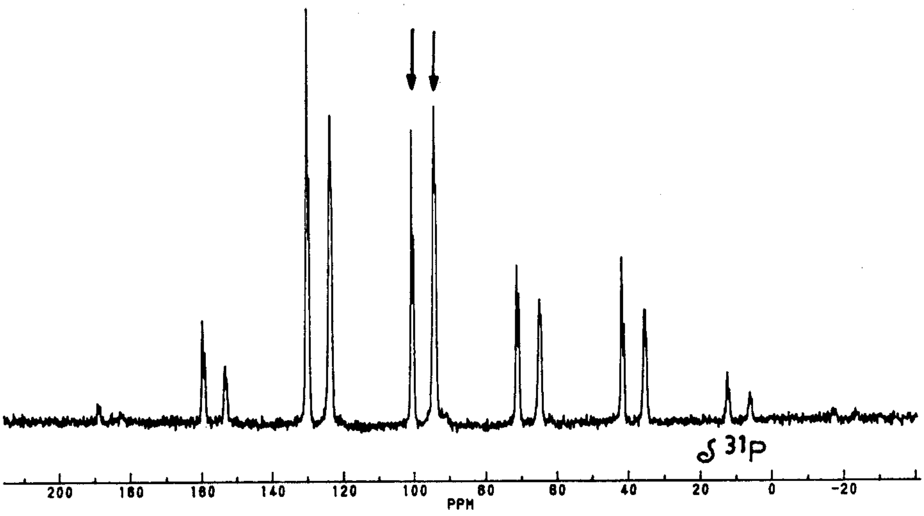


FIGURE 3 121.5 MHz ^{31}P CP/MAS NMR spectrum of solid $^{t}Bu_2P(S)(NSN)P(S)^{t}Bu_2$ (**3a**) (24 scans, recycle delay 5 s, contact time 5 ms, spinning speed 3568 Hz, temperature 283 K). The two centre bands according to E and Z position are marked by arrows. The splitting of the centre bands is due to non-averaged scalar and dipolar ^{31}P—^{14}N interactions.[11] The ^{31}P CP/MAS NMR spectrum of the analogous selenide **4a** is almost identical.

the coupling constant $^{1}J(^{31}P^{15}N)$ = 62.5 Hz has been determined by direct ^{15}N INEPT measurements[7] and HEED experiments.[6a] Negative contributions to $^{1}K(^{31}P^{15}N)$ arise mainly from the influence of lone electron pairs (lp) at phosphorus and nitrogen.[13] It has been shown that these negative contributions become much smaller if the phosphorus lp is engaged in bonding as in P(V)—N compounds. Thus, large and positive $^{1}J(^{31}P^{15}N)$ values in the P(III)—N compounds usually become small and may even change sign in P(V)—N compounds. A typical series is shown in the following sequence[14]:

$Me_2P(E)$—NHPh; E =	lp,	Te,	Se,	S,	Me^{+},	O
$^{1}J(^{31}P^{15}N)$ [Hz]	+53.0,	+36.0,	+16.5,	+11.3,	+4.1,	−0.5

Analogous changes have been observed for $^{1}J(^{31}P^{15}N)$ in N-pyrrolyl-phosphorus compounds,[15] where the nitrogen lp is part of the heteroaromatic ring system. However, the $^{1}J(^{31}P^{15}N)$ values of the compounds **1** to **4a** are close to those of the phosphinyl sulfur diimides with P(III) and do not show the systematic variation which has been observed for other P(III)—N and P(V)—N compounds. A change of the sign of $^{1}J(^{31}P^{15}N)$ in **1** to **4a** with respect to that determined for P(III)—N compounds is unlikely because of the small variation in the magnitude of the $^{1}J(^{31}P^{15}N)$ values and because of the magnitude of the isotope-induced shifts $^{1}\Delta^{15/14}N(^{31}P)$ (vide infra). Thus, these are the first examples of P—N compounds where sign and magnitude of $^{1}J(^{31}P^{15}N)$ are predominantly influenced by the electronic structure at the nitrogen atom.

One-Bond Isotope Shifts $^1\Delta^{15/14}N(^{31}P)$

The one-bond isotope shifts $^1\Delta^{15/14}$N(^{31}P) are negative (i.e., the ^{31}P NMR signals are shifted to lower frequencies) which is the general trend upon substitution with a heavier isotope.[16] The magnitude of these shifts is difficult to predict, in particular for large molecules, since the quantities of dynamic and electronic factors are unknown and may even be of opposite sign. Assuming that the dynamic factors are fairly constant for the series of related compounds **1** to **4a**, it is possible to inspect the data in Table II for general trends outlined previously.[16] There is a correlation between $^1\Delta^{15/14}$N(^{31}P) and δ^{31}P(^{t}Bu$_2$P) values, except for compounds **1a**, **c** and **2**. Considering the dependence on net charge at phosphorus, smaller $|^1\Delta^{15/14}$N(^{31}P)$|$ values are expected for the sulfides and the selenide with respect to the carbonylmetal complexes, in agreement with the experimental data. The negative contribution of the phosphorus lp is evident from the value obtained for ^{t}Bu$_2$P(NSN)P^{t}Bu$_2$ $^1\Delta^{15/14}$N(^{31}P) $= -58$ ppb,[6a] which is more negative than in all compounds **1** to **4a**. Although there is no satisfactory linear relationship between $^1J(^{31}P^{15}N)$ and $^1\Delta^{15/14}$N(^{31}P) values, an inversion of the sign of $^1J(^{31}P^{15}N)$ in **1** to **4a** as compared to the parent P(III)—N compounds such as ^{t}Bu$_2$P(NSN)P^{t}Bu$_2$, can be ruled out.

EXPERIMENTAL

All compounds were handled in an atmosphere of dry argon, and carefully dried solvents were used for syntheses and for preparation of the samples for NMR measurements. The starting materials,[11] the carbonylmetal complexes,[5] the disulfide[4] and diselenide[4] were prepared according to literature procedures.

Synthesis of the thiophosphinyl sulfur diimides (3b–3e).

General procedure: A freshly prepared solution of 3 mmoles of the phosphinyl sulfur diimide in 100 ml THF was treated with 200 mg (6.25 mmoles) of sulfur at 0°C. The colour of the solution rapidly changed from deep red to orange. After stirring at 0°C for two hours the solvent was removed at room temperature in vacuo. The product was extracted with 150 ml of pentane, filtered over sodium sulfate, and the solvent was removed from the filtrate. The moisture-sensitive compounds can be recrystallized from the solvents given below.

(Di-tert-butylthiophosphinyl)(di-iso-propylthiophosphinyl)sulfur diimide (**3b**). Orange crystals from pentane; m.p. 68–70°; yield 71.0% (820 mg), $C_{14}H_{32}N_2P_2S_3$, M = 386.564 g/mol; m/e = 386 (M$^+$, 100%).

(Di-tert-butylthiophosphinyl)(dicyclohexylthiophosphinyl)sulfur diimide (**3c**). Orange crystals from ether/benzene; m.p. 107–109°C; yield 7.2% (100 mg); $C_{20}H_{40}N_2P_2S_3$, M = 466.694 g/mol; m/e = 466 (M$^+$, 100%).

(Di-tert-butylthiophosphinyl)[tert-butyl(phenyl)thiophosphinyl]sulfur diimide (**3d**). Orange powder from hexane/dichloromethane; m.p. 157–161°C; yield 48.1% (620 mg); $C_{18}H_{32}N_2P_2S_3$, M = 434.608 g/mol; m/e = 434 (M$^+$, 100%).

(Di-tert-butylthiophosphinyl)(diphenylthiophosphinyl)sulfur diimide (**3e**). Orange powder from pentane/THF; m.p. 83–85°C; yield 67.0% (910 mg); $C_{20}H_{28}N_2P_2S_3$, M = 454.598 g/mol; m/e = 454 (M$^+$, 100%).

IR spectra: Perkin-Elmer 983 G, KBr disks
EI-MS: Finnigan MAT 8500 (Ionization energy 70eV, direct inlet).

NMR spectra in solution were recorded with Jeol FX90Q, Bruker AC 300 and Bruker AM 500 instruments. HEED pulse sequences were optimized as described.[6a] One-bond isotope shifts $^1\Delta^{15/14}$N(^{31}P) were determined by measuring the shift difference between the centre of the ^{15}N satellite signals and the centre of the ^{31}P resonance for the ^{31}P—^{14}N isotopomer as obtained by line shape analysis. A Bruker MSL 300 instrument served for recording solid state ^{31}P CP/MAS NMR spectra of samples packed in air-tight inserts[17] which fit exactly into the commercial ZrO_2 rotors. Isotropic solid state $\delta^{31}P$ data were assigned by running the ^{31}P CP/MAS NMR spectra at two different spinning speeds. All $\delta^{31}P$ values are given relative to external 85% H_3PO_4.

ACKNOWLEDGEMENTS

This work has been supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. E. K. thanks the Alexander-von-Humboldt-Stiftung for a fellowship. We thank Dr. A. Sebald and Dipl.-Chem. J. Kümmerlen (Bayerisches Geoinstitut, Universität Bayreuth) for measuring solid state ^{31}P CP/MAS NMR spectra.

REFERENCES

1. a) M. Herberhold, W. Bühlmeyer, A. Gieren, T. Hübner and J. Wu, *J. Organomet. Chem.*, **321,** 51 (1987); b) T. Chivers, C. Lensink and J. F. Richardson, *J. Organomet. Chem.*, **325,** 169 (1987); c) T. Chivers, C. Lensink and J. F. Richardson, *Organometallics,* **5,** 819 (1986); d) T. Chivers, C. Lensink and J. F. Richardson, *Organometallics,* **6,** 1904 (1987); e) T. Chivers, C. Lensink and J. F. Richardson, *Phosphorus and Sulfur,* **30,** 189 (1987).
2. M. Herberhold, W. Bühlmeyer, A. Gieren and T. Hübner, *J. Organomet. Chem.*, **321,** 37 (1987).
3. M. Herberhold and K. Schamel, *J. Organomet. Chem.*, **346,** 13 (1988).
4. M. Herberhold, W. Ehrenreich, A. Gieren, H. Betz and T. Hübner, *Chem. Ber.*, **118,** 1476 (1985).
5. M. Herberhold, S. M. Frank and B. Wrackmeyer, *J. Organomet. Chem.*, **410,** 159 (1991).
6. a) B. Wrackmeyer and E. Kupce, *J. Magn. Reson.*, in press; b) B. Wrackmeyer, E. Kupce and A. Schmidpeter, *Magn. Reson. Chem.*, **29,** 1045 (1991).
7. M. Herberhold, S. M. Frank and B. Wrackmeyer, *Z. Naturforsch.*, **43b,** 985 (1988).
8. a) G. A. Morris and R. Freeman, *J. Am. Chem. Soc.*, **101,** 760 (1979); b) D. P. Burum and R. R. Ernst, *J. Magn. Reson.*, **39,** 163 (1980); c) G. A. Morris, *J. Magn. Reson.*, **41,** 185 (1980).
9. D. T. Pegg, D. M. Doddrell and M. R. Bendall, *J. Chem. Phys.*, **77,** 2745 (1982).
10. B. Wrackmeyer, E. Kupce, G. Kehr and J. Schiller, *Magn. Reson. Chem.*, in press.
11. a) S. J. Opella, M. H. Frey and T. A. Cross, *J. Am. Chem. Soc.*, **101,** 5856 (1979); b) C. L. Groombridge, R. K. Harris, K. J. Packer, B. J. Say and S. F. Tanner, *J. Chem. Soc. Chem. Commun.*, **1980,** 174; c) A. C. Olivieri, L. Frydman and L. E. Diaz, *J. Magn. Reson.*, **75,** 50 (1987).
12. a) M. Witanowski, L. Stefaniak and G. A. Webb, *Annual Rep. NMR Spectrosc.*, **18,** 1 (1986); b) G. J. Martin, M. L. Martin and J.-P. Gousenard, in NMR—Basic Principles and Progress (edited by P. Diehl, E. Fluck and R. Kosfeld), vol. 18, Springer, Heidelberg 1981.
13. V. M. S. Gil and W. von Philipsborn, *Magn. Reson. Chem.*, **27,** 409 (1989).
14. W. McFarlane and B. Wrackmeyer, *J. Chem. Soc. Dalton Trans.*, **1976,** 2351.
15. B. Wrackmeyer, *Spectrochim. Acta* **40A,** 963 (1984).
16. C. J. Jameson, in Isotopes in the Physical and Biomedical Sciences (edited by E. Buncel and J. R. Jones), vol. 2, Elsevier, Amsterdam 1991, pp. 2–54.
17. L. H. Merwin, A. Sebald, I. E. Espidel and R. K. Harris, *J. Magn. Reson.*, **84,** 367 (1989).