3904 *Inorg. Chem.* **1996,** *35,* 3904−3912

Phosphorus Chemical Shift Tensors of Phosphole Derivatives Determined by ^{31}P NMR Spectroscopy of Powder Samples

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Received January 26, 1996[⊗]

The results of a systematic solid-state ^{31}P NMR study of 5-phenyldibenzophosphole, DBP, its chalcogenides, and some of its transition metal complexes are reported. Phosphorus chemical shift tensors have been obtained from ^{31}P NMR spectra of stationary samples and of samples spinning about the magic angle. The spans of the phosphorus chemical shift tensors for DBP and its chalcogenides are comparable to those of the corresponding compounds of triphenylphosphine; however, the asymmetry of the tensors for the DBP series reflects the reduced local symmetry at phosphorus. For the complexes $(DBP)M(CO)_5$ and *cis*-$(DBP)_2M(CO)_4$, where M is a group 6 transition metal (Cr, Mo, W), the most shielded component of the phosphorus shift tensor is found to be relatively independent of the metal or complex, $\delta_{33} = -41 \pm 8$ ppm, and is thought to lie along or close to the P−M bond axis direction. In contrast, δ_{11} and δ_{22} show considerable variation but decrease systematically on descending the group from Cr to W. Group 10 metal complexes, $(DBP)_2MX_2$, have also been investigated, including several trans geometric isomers of nickel, cis and trans isomers of palladium, and *cis* isomers of platinum. The phosphorus shift tensors are nonaxially symmetric with spans in the range 50 −150 ppm. The phosphorus shift tensors of the two nonequivalent DBP ligands of $(DBP)_2PtX_2$ (X = Cl, Br) exhibit quite different principal components. The intermediate component of the shift tensor is thought to lie along the Pt−P bond in these complexes. Some of the complexes exhibit interesting MAS-frequency-dependent ^{31}P NMR spectra.

Introduction

The literature on isotropic phosphorus chemical shifts, $\delta(^{31}\mathrm{P})$, determined from ^{31}P nuclear magnetic resonance (NMR) studies of solutions abounds,[1] and for closely related compounds, empirical correlations of $\delta(^{31}\mathrm{P})$ against virtually any other structural, physical, biological, *etc.* parameter exist.[1,2] However, the theoretical underpinnings of these apparent relations are generally not understood. In fact, it is fair to claim that phosphorus chemical shifts are not well understood. As a first step in improving our understanding of chemical shifts, it is our contention that it is necessary to investigate the chemical shift tensor rather than simply characterizing the trace of the tensor as in solution NMR studies. In this respect, solid-state NMR is not just the method of choice for the characterization of insoluble materials but it is also a powerful tool for studying the chemical shift tensor of a nucleus in well-defined molecular compounds. Another advantage of solid-state studies is that one can often use single-crystal diffraction techniques to define the structure of the compounds of interest. In contrast, the precise structure or conformation of a compound may not be known in solution.

Although the number of papers on phosphorus chemical shift tensors is growing steadily,[3] the data are frequently too heterogeneous to develop well-established, valuable empirical benchmarks. For example, there are not many data on phosphorus chemical shift tensors of a specific phosphine ligand in a wide variety of different chemical environments. In the present study, we systematically focus on a selection of phosphole compounds. Phospholes are of ongoing special theoretical and chemical interest in organic and inorganic chemistry.[4−6] The extent of delocalization of the electron lone pair at phosphorus into the phosphole ring system has been a question of considerable debate and appears, now, to have been settled.[6] Initially, $\delta(^{31}\mathrm{P})$ served as an argument in favor of the delocalization hypothesis. This was, however, based on misconceptions[7] and emphasizes the importance of gaining a deeper understanding of the factors affecting phosphorus chemical shifts. The most promising approach seems to combine experimental and theoretical investigations of the chemical shift

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[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1996.

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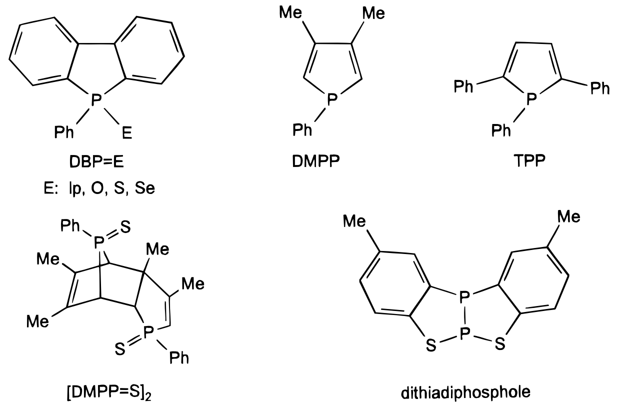
S0020-1669(96)00095-X CCC: $12.00

Chart 1



tensor. Unfortunately, while the experimental characterization of chemical shift tensors and the theoretical calculation[8] of phosphorus chemical shift tensors for small molecules containing first- and second-row elements are relatively straightforward, the rationalization of the results remains a challenge. Here, we present the results of a comprehensive experimental ^{31}P NMR investigation of DBP (Chart 1), its chalcogenides, and a series of its metal complexes. Data for some other solid phospholes and their derivatives are also presented.

Experimental Section

The preparation of the phosphole derivatives has been published previously.[9−11] Solid-state ^{31}P NMR experiments were carried out using Bruker MSL-200 (B_0 = 4.7 T) and AMX-400 (B_0 = 9.4 T) spectrometers. Phosphorus-31 cross-polarization magic-angle spinning (CP/MAS) NMR spectra were acquired using Bruker double-bearing MAS probes, with 3.5 μs proton pulse widths, contact times of 3−5 ms, and recycle delays of 20−60 s. Chemical shifts were referenced with respect to external 85% aqueous H_3PO_4 by setting the peak of external solid $NH_4H_2PO_4$ to 0.8 ppm. Phosphorus chemical shifts may be converted to absolute shieldings by using the following expression: $\sigma = 328.35\ \text{ppm} - \delta$.[12] The analysis of the spinning-sideband intensities in the MAS NMR spectra was carried out using the computer program HBA, a nonlinear least-squares routine based on extended Herzfeld−Berger tables.[13] In cases where spectra of static powder samples were available, the parameters obtained from the MAS spectra were refined using the first derivative of the absorption line shape of the static powder pattern. Calculation of the MAS and static powder patterns was performed using WSolids, a computer program developed in this laboratory utilizing the C++ language. All calculations were carried out using a 80486 microprocessor.

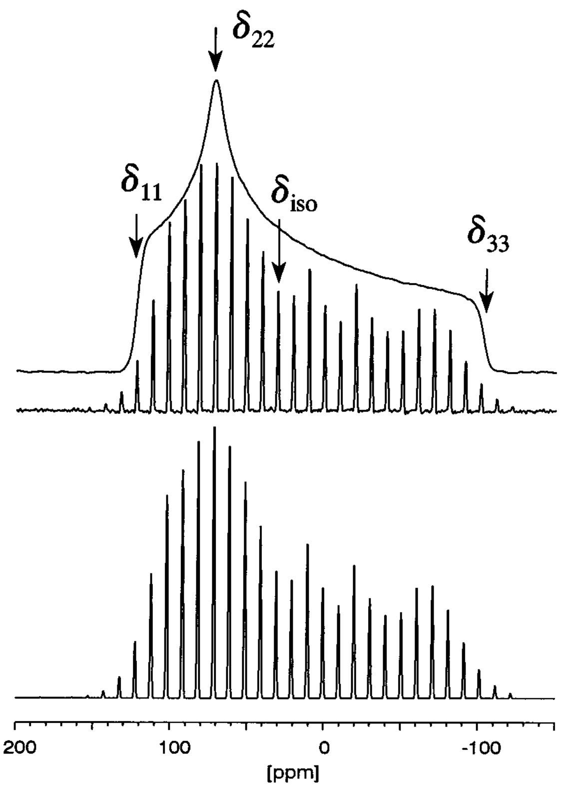


Figure 1. ^{31}P CP NMR spectra of a powder sample of anhydrous DBP=O. Top trace: stationary sample, 2828 scans, 30 s recycle delay. Middle trace: magic-angle spinning at 824 Hz, 128 scans, 20 s recycle delay. Bottom trace: MAS spectrum calculated using the parameters given in Table 1.

Results and Discussion

In general, the chemical shift of a particular nucleus depends on the orientation of the molecule with respect to the external magnetic field. For NMR spectra of stationary powder samples, this typically results in broad line shapes, as illustrated in Figure 1 for the ^{31}P NMR spectrum of 5-phenyldibenzophosphole 5-oxide. The characteristic features of this chemical shift (CS) anisotropy powder pattern are directly related to the principal components of the CS tensor:[14] the chemical shifts of the points of inflection at the high- and low-frequency ends give δ_{11} and δ_{33}, respectively, while the position of the singularity corresponds to δ_{22}. Magic-angle spinning of the sample introduces considerable line narrowing, resulting in a sharp peak at the average value of the three principal components, the isotropic chemical shift, $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$.[15] At spinning frequencies lower than the total width of the CS powder pattern, the isotropic peak is flanked by spinning sidebands at integral multiples of the spinning frequency ($\pm n\nu_r$). The shape of the envelope of spinning sideband intensities at slow spinning rates mimics the line shape of the static powder pattern and allows one to extract the principal components from its analysis.[13a,16]

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Table 1. Phosphorus Chemical Shift Tensors (ppm) and Spin−Spin Coupling Constants (Hz) of Phospholes and Their Chalcogenides As Determined by ^{31}P CP NMR Studies of Powder Samples, and Comparison with Other Phosphine Derivatives[a]

compd[b]	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Ω[c]	J
DBP	−17.1	12	−19	−45	57	
	−18.3	9	−21	−45	54	
DBP=O	31.1	124	72	−102	226	
DBP=O·H_2O	35.3	117	68	−78	195	
DBP=S	40.4	118	61	−57	175	
DBP=Se	29.3	96	36	−45	141	732[d]
	28.2	99	47	−61	160	765[d]
$[DMPP{=}S]_2$	109.8	246	104	−22	268	38[e]
	60.7	148	81	−47	195	38[e]
PMe_3[f]	−63	−61	−61	−68	7	
PPh_3[g]	−10	9	9	−42	51	
TPP[g]	1	30	−6	−22	52	
PCy_3[g]	7	35	18	−30	75	
dithiadiphosphole[h]	52 (PC_2)	190	25	−54	244	
	76 (PS_2)	129	122	−25	154	
$Me_3P{=}O$[i]	36	102	102	−96	198	
$Ph_3P{=}O$[j]	32	97	97	−98	195	
$Me_3P{=}S$[i]	59	87	87	4	83	
$Ph_3P{=}S$[i]	43	107	86	−64	173	
TEPS[k]	51	108	98	−54	162	
$Me_3P{=}Se$[i]	8	37	37	−49	86	
$Ph_3P{=}Se$[i]	33	98	56	−55	153	

[a] Chemical shifts are reported with respect to 85% aqueous H_3PO_4, with positive values indicating shifts toward higher frequencies. Errors in the principal components of the chemical shift tensors are estimated to be 2 ppm; errors in the coupling constants, to be 5 Hz. [b] See Chart 1. [c] Span of the chemical shift tensor, $\Omega = \delta_{11} - \delta_{33}$. [d] $^1J(^{77}Se,^{31}P)$. [e] $^3J(^{31}P,^{31}P)$. [f] Reference 19. [g] Reference 20. [h] Reference 21. [i] Reference 25. [j] Reference 16. [k] Reference 27.

The bottom trace of Figure 1 shows a spectrum calculated using the values given in Table 1. From NMR spectra of powder samples, there is no information available on the orientation of the CS tensor in the molecular frame of reference, unless spin−spin interactions offer an internal frame of reference (*vide infra*).[17]

Phospholes and Their Chalcogenides. Phosphorus NMR data obtained for phospholes and some of their chalcogenides are summarized in Table 1. Related data for phosphines and some of their chalcogenides are included for comparison. Representative ^{31}P NMR spectra of stationary powder samples of phospholes and their derivatives are shown in Figure 2. In most cases, the spectra obtained with MAS contained more than one isotropic peak, indicating the presence of more than one phosphorus site in the asymmetric unit. In order to facilitate the discussion, the ^{31}P NMR spectra of each compound will be described separately.

(a) 5-Phenyldibenzophosphole, DBP. DBP can be considered as a constrained triphenylphosphine, where two of the phenyl rings are annealed in the ortho positions (Chart 1). This results in a lowering of the molecular symmetry due to the relatively small endocyclic C−P−C angle. DBP crystallizes in the orthorhombic space group $Pbc2_1$ with eight molecules in the unit cell.[18] The asymmetric unit consists of two independent molecules with almost identical structures. For example, the endocyclic C−P−C angles for the two molecules are 88.9(4) and 89.5(4)°, and the C−P−C−C torsional angles of the envelope conformation are 32.0(5) and 34.1(6)°. Consistent with the crystal structure, the ^{31}P CP/MAS NMR spectrum exhibits two peaks of equal intensities and almost identical isotropic chemical shifts, −17.1 and −18.3 ppm. In addition, the principal components of the two chemical shift tensors are essentially identical. In Table 1, we compare the CS tensor components of DBP with those of some other phosphines, namely trimethylphosphine, PMe_3,[19] tricyclohexylphosphine, PCy_3, triphenylphosphine, PPh_3, 1,2,5-triphenylphosphole, TPP,[20] and a butterfly-like dithiadiphosphole[21] (Chart 1). Compared to that of PPh_3, the isotropic chemical shift of DBP indicates a slightly higher shielding of phosphorus by approximately 8 ppm. As Table 1 reveals, this difference is mainly associated with a change in δ_{22}. According to the local molecular symmetry about phosphorus in PPh_3, it is generally assumed[20] that the direction of highest shielding is along the direction of the approximate C_3 axis. Therefore, it might appear that the increase in shielding along the direction of δ_{22} in DBP is associated with one of the directions perpendicular to the approximate local C_3 axis. However, in the case of DBP, the assumption of local C_3 symmetry is inappropriate, as the endo- and exocyclic C−P−C angles are on the order of 90 and 103°, respectively.[18] This asymmetry is also reflected in the CS tensor, as δ_{11} and δ_{22} differ by roughly 30 ppm! In TPP (Chart 1), this asymmetry

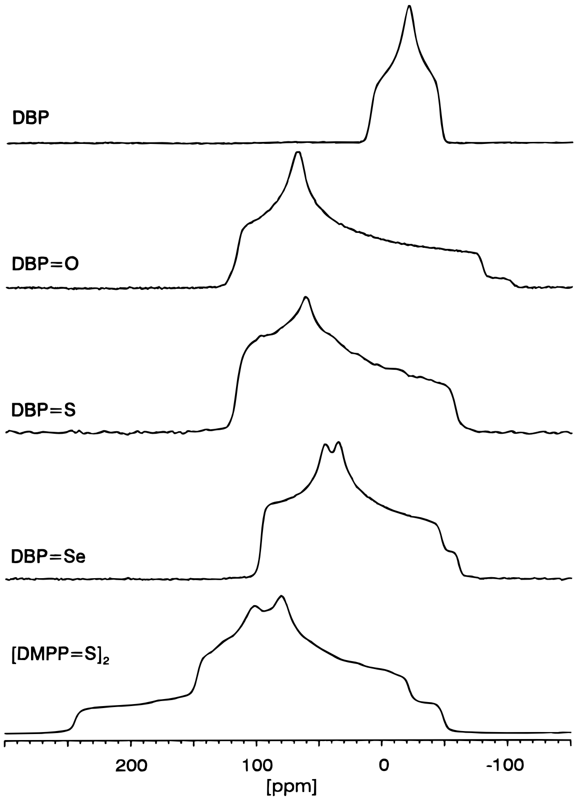

Figure 2. ^{31}P CP NMR spectra of stationary powder samples: DBP, 865 scans, 60 s recycle delay; DBP=O and its hydrate, 1188 scans, 60 s recycle delay; DBP=S, 1057 scans, 60 s recycle delay; DBP=Se, 718 scans, 60 s recycle delay; $[DMPP{=}S]_2$, 4011 scans, 20 s recycle delay.

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is further enhanced. Indeed, as the crystal structure indicates, the average of the exocyclic C−P−C angles is 105°.[22] A dramatic change in the chemical shift tensor components occurs if phosphorus participates simultaneously in two phosphole rings, as demonstrated by the dithiadiphosphole also depicted in Chart 1. Compared to that of DBP, the value of δ_{11} changes substantially. Using dipolar-chemical shift NMR spectroscopy of the ^{31}P−^{31}P spin pair in the dithiadiphosphole, Wu *et al.*[21] were able to determine the orientation of the chemical shift tensor relative to the dipolar tensor. They found that the orientation of δ_{11} is approximately parallel to the P−P direction and hence perpendicular to the presumed direction of the lone pair at phosphorus. The importance of the lone pair of electrons at phosphorus in controlling the chemical shielding characteristics of phosphole and the phospholide anion was discussed recently by Chesnut and Quin.[7] The phosphorus nucleus in the phospholide is deshielded by about 80 ppm compared to the parent phosphole. According to Chesnut and Quin, the lone pair of electrons at the pyramidal phosphorus of phospholes is barely conjugated with the ring system. In contrast, for the phospholide anion the lone pair perpendicular to the molecular plane is essentially fully conjugated. However, the difference in $\delta(^{31}\mathrm{P})$ arises not from the different amount of conjugation but rather from contributions from the **in-plane** lone pair, which is absent in the phosphole (*i.e.*, the in-plane lone pair of the phospholide is stabilized in phosphole by formation of a P−H bond).

(b) 5-Phenyldibenzophosphole 5-Oxide, DBP═O. Initially, the ^{31}P CP/MAS NMR spectrum of DBP═O exhibited two peaks, a strong peak at 35.3 ppm and a weaker peak at 31.1 ppm (the chemical shift in $CHCl_3$ solution is 33.2 ppm). Over a period of days, the relative intensity of the weaker peak increased. The chemical shift tensors of both species are typical of tertiary phosphine oxides, and subsequent analysis revealed the peak at $\delta_{iso} = 35.3$ ppm to be due to the DBP═O hydrate. Figure 2 shows a spectrum due to a mixture of both hydrate and anhydrous DBP═O, while Figure 1 displays the spectrum of the anhydrous form. Other tertiary phosphine oxides are known to crystallize as hydrates, even when crystallized from solvents other than water, *cf.* tris(2,4,6-trimethoxyphenyl)phosphine oxide.[23] The inclusion of water in phosphine oxides generally leads to hydrogen bonding between water and the P═O unit. Comparison of the data for anhydrous DBP═O and the hydrate in Table 1 demonstrates that the effect of hydration is primarily expressed in the value of δ_{33}, which indicates that phosphorus is less shielded along the direction of the P═O bond in the hydrate by more than 20 ppm. Similarly, larger isotropic chemical shifts have been observed for cocrystals of triarylphosphine oxides with amines relative to the shifts observed for phosphine oxides.[24] It has been proposed that stronger hydrogen bonding between the amine and the P═O moiety results in greater deshielding at phosphorus. The authors also concluded that in these systems other structural factors appear to have little effect on the isotropic ^{31}P chemical shift. The average values of δ_{11} and δ_{22} for both DBP═O hydrate and anhydrous DBP═O compare well to the values observed for other typical phosphine oxides, *e.g.*, Me_3P═O[25] and Ph_3P═O.[16b,26] While the phosphorus chemical shift tensor is axially symmetric for most of the common phosphine oxides, the results for DBP═O and for DBP═O hydrate indicate that there is no local C_3 axis at phosphorus in the latter compounds.

(c) 5-Phenyldibenzophosphole 5-Sulfide, DBP═S. The crystal structure of DBP═S is unavailable, but the ^{31}P CP/MAS NMR spectrum indicates the presence of only one magnetically distinct phosphorus site in the asymmetric unit. The isotropic chemical shift of the sulfide is 9 ppm to high frequency of that of DBP═O. This trend is well-documented for phosphine sulfides and their corresponding oxides.[1] As Table 1 indicates, this change in DBP═S is caused by shielding differences in δ_{33}, while δ_{11} and δ_{22} are essentially the same in both the phosphine oxide and the sulfide. Besides arguments employing local symmetry,[25,26] the orientation of the ^{31}P chemical shift tensor has been determined experimentally via single-crystal ^{31}P NMR of tetraethyldiphosphine disulfide[27] and tetrabutyldiphosphine disulfide.[28] In both cases, the most shielded direction (*i.e.*, that associated with δ_{33}) is very close to the direction of the P═S bond. With the notable exception of Me_3P═S (Table 1), the value of δ_{33} in most phosphine sulfides is approximately −60 ppm.

(d) 5-Phenyldibenzophosphole 5-Selenide, DBP═Se. DBP═Se crystallizes in the monoclinic space group $P2_1/n$ with eight molecules in the unit cell.[29] There are two independent molecules in the asymmetric unit, which differ mainly in the orientation of the phenyl ring. The P−Se distances are 2.110(2) and 2.086(3) Å, comparable to the values found for Ph_3P═Se (2.106(1) Å)[30] and tri-*m*-tolylphosphine selenide (2.109(5) Å).[31] The ^{31}P CP/MAS NMR spectrum of DBP═Se indicates two unique phosphorus sites, consistent with the known crystal structure.[29] The ^{31}P NMR spectrum of the static powder sample, shown in Figure 2, indicates that the chemical shift tensors at each site differ. Since the site with greatest shielding along the direction of δ_{33} is also associated with the larger $^{1}J(^{77}\mathrm{Se},^{31}\mathrm{P})$, we tentatively assign this species to the crystallographic site with the slightly shorter P−Se distance (the chemical shift and $^{1}J(^{77}\mathrm{Se},^{31}\mathrm{P})$ in solution are 27.0 ppm and $J = 751$ Hz, respectively). Unfortunately, few data on phosphine selenides are available,[25] but the comparison with Ph_3P═Se shows that the ^{31}P CS tensors of both compounds are quite similar. It is interesting that the local symmetry at the phosphorus of both DBP═Se and Ph_3P═Se[30] seems to be distorted considerably from C_3. This is also reflected in the difference in δ_{11} and δ_{22} in both compounds.

(e) 3,4-Dimethyl-1-phenylphosphole 1-Sulfide Dimer, [DMPP═S]$_2$. This compound is the [4+2] Diels−Alder dimer of the sulfide of DMPP, 3,4-dimethyl-1-phenylphosphole (Chart 1). Two different phosphorus sites are evident from the ^{31}P CP/MAS NMR spectrum, and as Figure 2 demonstrates, both phosphorus nuclei differ in their chemical shift anisotropies. Upon dimerization of DMPP═S, eight different endo or exo isomers may result. Two isomers of [DMPP═S]$_2$, one exo and the other endo, have been prepared by different synthetic routes.[32] From solution ^{31}P NMR, the chemical shifts were reported as 87.6 and 52.4 ppm, $^{3}J(^{31}\mathrm{P},^{31}\mathrm{P}) \approx 0$ Hz, for the exo

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Table 2. Phosphorus Chemical Shift Tensors (ppm) and Spin−Spin Coupling Constants (Hz) of 5-Phenyldibenzophosphole (DBP) Complexes of Chromium, Molybdenum, and Tungsten Carbonyls[a]

compd	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Ω^b	${}^1J$(M,P)
(DBP)Cr(CO)$_5$	46.8	127	41	−28	155	
(DBP)Mo(CO)$_5$	28.0	104	24	−44	148	120^c
(DBP)W(CO)$_5$	7.7	69	−13	−36	105	
cis-(DBP)$_2$Cr(CO)$_4$	52.4	119	75	−39	158	
	43.8	124	44	−34	158	
cis-(DBP)$_2$Mo(CO)$_4$	33.3	89	50	−40	129	128^c
	24.5	102	12	−40	142	128^c
cis-(DBP)$_2$W(CO)$_4$	14.4	56	25	−39	95	216^d
	3.7	70	−21	−38	108	222^d
fac-(DBP)$_3$W(CO)$_3$	12.7	72	29	−63	135	216^d
	8.7	70	−3	−42	112	222^d
	3.3	66	−15	−46	112	205^d

[a] Chemical shifts are reported with respect to 85% aqueous H_3PO_4, with positive values indicating shifts toward higher frequencies. Errors in the principal components of the chemical shift tensors are estimated to be 2 ppm; errors in the coupling constants, to be 5 Hz. [b] Span of the chemical shift tensor, $\Omega = \delta_{11} - \delta_{33}$. [c] ${}^1J({}^{95/97}\text{Mo},{}^{31}\text{P})$. [d] ${}^1J({}^{183}\text{W},{}^{31}\text{P})$.

isomer, and 103.8 and 57.6 ppm, ${}^3J({}^{31}\text{P},{}^{31}\text{P}) = 45$ Hz, for the endo isomer. The chemical shifts in solution of the isomer studied here are 108.8 ppm for the bridging Ph−P═S group and 62.1 ppm for the regular phosphole sulfide group, with ${}^3J({}^{31}\text{P},{}^{31}\text{P}) = 44$ Hz.[32] On the basis of these data, we anticipate an endo geometry for the compound studied here. The major structural difference between the endo and exo isomers with regard to phosphorus appears to be the endocyclic C−P−C angle at the bridging Ph−P═S unit. It has been shown in the case of a molybdenum complex of an exo isomer that this angle is significantly smaller, 79°, than in a related compound with endo configuration, which shows an endocyclic C−P−C angle of 87°.[33]

The phosphorus chemical shift anisotropy of the phosphole sulfide moiety is similar to that found for DBP═S, except for an additional deshielding of 10−30 ppm along each of the principal components. However, the phosphorus of the bridging Ph−P═S exhibits a remarkable deshielding along the direction of δ_{11}, which is clearly the greatest deshielding observed for any of the phosphole compounds studied here. The DMPP═S dimer is similar to the 7-phosphanorbornenes, which have been the subject of a recent *ab initio* MO study[34] because of the unusual deshielding of the bridging phosphorus. The authors of this study demonstrated that the calculated phosphorus shielding in this case is related in a simple way to the HOMO−LUMO energy gap. The substituent or lone-pair orbital at phosphorus can interact with the π-system of the C═C bond of the norbornene framework—an interaction which is also very dependent on the syn or anti configuration of the substituent with respect to this double bond.

Complexes of DBP with Chromium, Molybdenum, and Tungsten Carbonyls. Phosphorus NMR data obtained for complexes formed by the reaction of DBP with Cr, Mo, and W hexacarbonyls are summarized in Table 2. Before discussing the phosphorus chemical shift tensors obtained for these complexes, we comment on the measured J(M,P) values.

(a) Indirect Spin−Spin Coupling Constants. Each element of the sixth transition metal group possesses at least one NMR-active isotope. While indirect coupling to the spin $^1/_2$ isotope ^{183}W (14.40%, $\gamma = 1.1283 \times 10^7$ rad s^{-1} T^{-1}) is routinely observed in ^{31}P NMR spectra of solutions, the observation of couplings involving ^{53}Cr ($I = {}^3/_2$, 9.55%, $\gamma = -1.50770 \times 10^7$ rad s^{-1} T^{-1}) and ${}^{95/97}$Mo (^{95}Mo: $I = {}^5/_2$, 15.72%, $\gamma = -1.7514 \times 10^7$ rad s^{-1} T^{-1}; ^{97}Mo: $I = {}^5/_2$, 9.46%, $\gamma = -1.7884 \times 10^7$ rad s^{-1} T^{-1}) is usually limited to reports from NMR spectra of the corresponding metal.[35] Of these, couplings to ^{95}Mo are most common since it has the smallest nuclear quadrupole moment, $Q = -0.022 \times 10^{-28}$ m^2, compared to those of ^{97}Mo, $Q = 0.255 \times 10^{-28}$ m^2, and ^{53}Cr, $Q = -0.15 \times 10^{-28}$ m^2.[36] Generally, these nuclei relax efficiently *via* the quadrupolar mechanism. Because of their short relaxation times, they are often efficiently decoupled from ^{31}P in NMR studies of solutions. In the solid state, the quadrupolar relaxation times are generally much longer. This effect is offset by the broader ^{31}P NMR peaks, making the detection of small satellite peaks difficult. ^{183}W and ${}^{95/97}$Mo satellites have been observed in ^{31}P CP/MAS NMR spectra.[37] Phosphorus NMR spectra of solid *cis*-(DBP)$_2$Mo(CO)$_4$ provide a particularly nice example of ${}^{95/97}$Mo satellites in ^{31}P MAS spectra (Figure 3). The values of coupling constants determined in the present study are typical of ${}^1J$(M,P) coupling constants involving molybdenum and tungsten. Coupling constants involving ^{53}Cr are expected to be smaller than those of higher homologues,[1b,38] and this may explain the lack of evidence for satellites in the ^{31}P CP/MAS spectra obtained. Small couplings would undoubtedly be masked by the strong central peak due to uncoupled ^{31}P (90.45%).

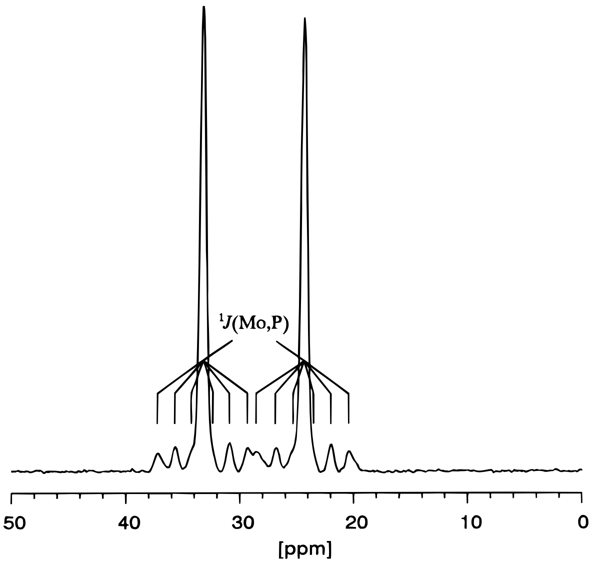

Figure 3. Isotropic peaks in the ^{31}P CP/MAS NMR spectrum of *cis*-(OC)$_4$Mo(DBP)$_2$, showing the presence of ${}^{95/97}$Mo satellites.

(b) Phosphorus Chemical Shift Tensors. The phosphorus chemical shift tensor data obtained for DBP-substituted chromium, molybdenum, and tungsten carbonyls are summarized in Table 2. Upon coordination, the ^{31}P nucleus generally becomes more deshielded compared to that of the free phosphine ligand; the difference in the chemical shift of the coordinated ligand and the free ligand is often referred to as a coordination

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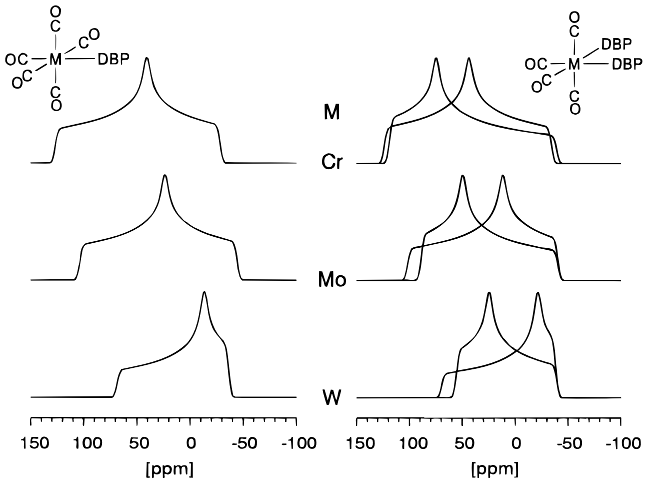

Figure 4. Schematic ^{31}P chemical shift powder patterns observed for the complexes (DBP)M(CO)$_5$, left, and *cis*-(DBP)$_2$M(CO)$_4$, right, where M = Cr (top), Mo (middle), and W (bottom).

shift.[10,39] The isotropic chemical shifts follow the trend known from many ^{31}P NMR solution studies; *viz.*, as one descends within the same group, the phosphorus nucleus becomes more shielded.[1b] On average, there is an increase in shielding of 20 ppm between Cr and Mo and between Mo and W. The orientation of phosphorus CS tensors in metal phosphine complexes has been determined experimentally for only a few complexes of molybdenum,[40] platinum,[41,42] rhodium,[43] mercury,[44] indium,[45] and manganese,[46] using either single-crystal or dipolar-chemical shift NMR techniques. In many of these complexes, the principal component with chemical shifts of −20 to −40 ppm roughly corresponds to the direction of the M−P bond; in many (but not all!) examples, this is also the direction of highest shielding. For all complexes in Table 2, δ_{33} more or less remains at -41 ± 8 ppm and is thought to be oriented along or close to the M−P bond. This is similar to the value observed for the free ligand at this orientation. The invariability of δ_{33} is also illustrated in Figure 4, where, for ease of comparison, schematic powder patterns of the (DBP)M(CO)$_5$ and *cis*-(DBP)$_2$M(CO)$_4$ series of complexes are shown. The ^{31}P CP/MAS spectra of the *cis*-(DBP)$_2$M(CO)$_4$ series indicate two nonequivalent DBP ligands, which, in the case of *cis*-(DBP)$_2$Cr(CO)$_4$, has been verified by X-ray diffraction.[10] In contrast to the insensitivity of δ_{33}, the two other principal components of the phosphorus chemical shift tensor change in a characteristic and almost constant manner to lower frequencies on descending the group, *viz.*, by 17−32 ppm from Cr to Mo and by 25−37 ppm from Mo to W. Such effects have been observed previously in ^{31}P NMR spectra of molybdenum and tungsten phosphine complexes[37,42] and are analogous to changes in carbon chemical shift tensors of the hexacarbonyls.[47] Clearly, variations in δ_{11} and δ_{22} are responsible for the changes in the coordination shift of these complexes. The sensitivity of the chemical shift components perpendicular to the M−P bond (*i.e.*, δ_{11} and δ_{22}) to the nature of the metal is not unexpected. In Ramsey's formulation of nuclear magnetic shielding, the contribution of the paramagnetic term to shielding along a particular direction depends on how efficiently the angular momentum operator mixes orbitals in the plane perpendicular to that direction.[48] Hence, if the nature of the M−P bond changes, one would expect this to be reflected in the perpendicular components. Note, however, that this does not necessarily imply that the parallel component will be unaffected. The paramagnetic contribution to the direction along the metal−phosphorus bond should primarily arise from the mixing of orbitals involving the substituents at phosphorus. These orbitals may also be affected by the nature of the metal, and the shielding along the M−P bond may therefore change with the metal *via* an indirect mechanism. It is obvious that a detailed MO description of metal−phosphine complexes is required to fully understand the phosphorus shielding trends in these complexes.

One of the sites in each of the *cis*-(DBP)$_2$M(CO)$_4$ complexes exhibits a powder pattern which is remarkably similar to the one observed for the corresponding monosubstituted species. This similarity, however, appears to be coincidental. The crystal structures of (DBP)Cr(CO)$_5$ and *cis*-(DBP)$_2$Cr(CO)$_4$ reveal that the bond angles about phosphorus in the monosubstituted complex are sufficiently different from both of the sites in *cis*-(DBP)$_2$Cr(CO)$_4$, precluding any assignment based on structural similarities.

Finally, one of the sites of *fac*-(DBP)$_3$W(CO)$_3$ exhibits significantly higher shielding along the direction of δ_{33} compared to the case of the other complexes. Similar effects have been observed for *fac*-(etp)Mo(CO)$_3$[42] (etp = [Ph$_2$P(CH$_2$)$_2$]$_2$-PPh) and might be related to the shorter M−P distance found for one of the phosphine ligands.[49]

Complexes of Phospholes with Nickel, Palladium, and Platinum. Phosphorus NMR data for the nickel, palladium, and platinum complexes are given in Table 3.

(a) Complexes of Nickel. There are few data on ^{31}P chemical shifts for phosphine complexes of nickel, in general, and phosphole complexes, in particular.[4,5] The reason is that many complexes of nickel(II) are tetrahedral and paramagnetic rather than square-planar and diamagnetic or there might be rapid interconversion between both allogons.[50] There even are some examples known where both allogons exist in the solid state.[51]

The isotropic peak in the ^{31}P CP/MAS NMR spectrum of (DMPP)$_2$Ni(SCN)$_2$, Figure 5, shows one sharp peak flanked by smaller peaks appearing to be satellites, but much stronger in intensity than possible ^{61}Ni satellites ($I = {}^3/_2$, 1.19%). Furthermore, the relative intensities in the spinning sidebands is much higher and therefore typical of effects due to strong homonuclear spin−spin coupling.[52] This type of spectrum results from an AB-type coupling between two slightly nonequivalent phosphorus nuclei (at 9.4 T, the ^{31}P NMR spectrum

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Table 3. Phosphorus Chemical Shift Tensors (ppm) and Spin−Spin Coupling Constants (Hz) of 5-Phenyldibenzophosphole (DBP) and 1-Phenyl-3,4-dimethylphosphole (DMPP) Complexes of Nickel, Palladium, and Platinum[a]

compd	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	Ω^b	J
trans-$(DMPP)_2Ni(SCN)_2$	22.7	63	30	−22	85	334[c]
	20.2	55	18	−12	67	334[c]
trans-$(DBP)_2NiCl_2$	1.1, −2.9	(38)	(6)	(−45)	(83)	380[c]
trans-$(DBP)_2PdCl_2$	11.3	(41)	(17)	(−24)	(65)	530[c]
trans-$(DBP)_2PdBr_2$	10.1	(45)	(14)	(−27)	(72)	
trans-$(DMPP)_2PdBr_2$[d]	21.7	41	32	−8	49	
	18.7	53	20	−17	70	
cis-$(DMPP)_2PdBr_2$[d]	29.5	57	44	−12	69	
	25.8	69	30	−22	91	
trans-$(DBP)_2PdI_2$	−2.0	92	−28	−70	162	
cis-$(DBP)_2PdI_2$	8.6	64	25	−63	127	
cis-$(DBP)_2PtCl_2$	7.8	50	25	−52	102	3280[e]
	1.0	80	−11	−68	148	3575[e]
cis-$(DBP)_2PtBr_2$	7.0	54	25	−59	113	3216[e]
	0.2	83	−15	−65	148	3529[e]
cis-$(DBP)_2PtI_2$	−3.5	85	−33	−66	151	3357[e]
	−4.4	62	−29	−46	108	3264[e]

[a] Chemical shifts are reported with respect to 85% aqueous H_3PO_4, with positive values indicating shifts toward higher frequencies. Errors in the principal components of the chemical shift tensors are estimated to be 2 ppm; errors in the coupling constants, to be 5 Hz. Values given in parentheses are less accurate because of the presence of nearly identical, unresolved sites or neglect of homonuclear spin−spin interactions. [b] Span of the chemical shift tensor, $\Omega = \delta_{11} - \delta_{33}$. [c] $^2J(^{31}P,^{31}P)$. [d] Reference 56. [e] $^1J(^{195}Pt,^{31}P)$.

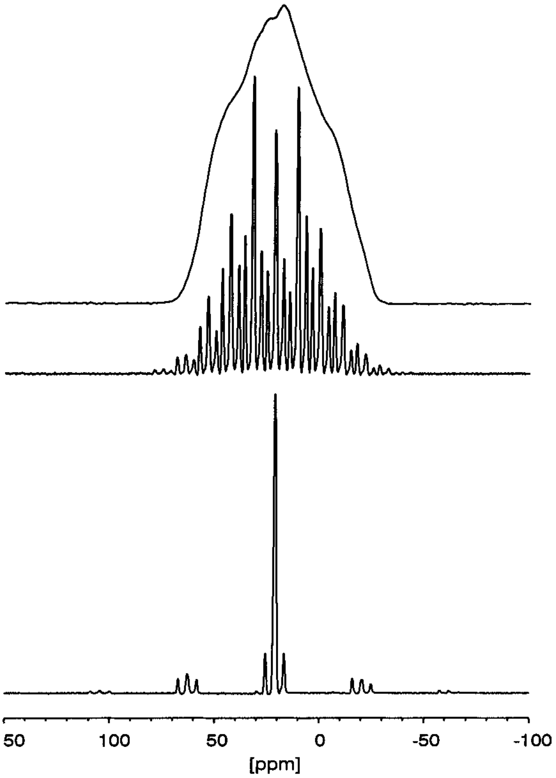

Figure 5. ^{31}P NMR spectra of powder samples of *trans*-$(DMPP)_2Ni(SCN)_2$. Top trace: stationary sample, 7528 scans, 10 s recycle delay. Middle trace: MAS spectrum at 878 Hz, 382 scans. Bottom trace: MAS spectrum at 3370 Hz, 56 scans.

is a typical AB spectrum). The $^2J(^{31}P,^{31}P)$ of 334 Hz is indicative of a trans arrangement of phosphole ligands. The ^{31}P chemical shift in $CDCl_3$ solution is 15.3 ppm, approximately 6 ppm less than the average value in the solid state.

For the DBP complexes of the nickel halides, only spectra of inferior quality could be obtained, in agreement with magnetic measurements indicating large μ_{eff} (2.9 μ_B). The exception, however, is the brown form of $(DBP)_2NiCl_2$,[11a] which is diamagnetic. Its ^{31}P NMR spectrum is similar to that of $(DMPP)_2Ni(SCN)_2$ and shows only one peak at sample spinning frequencies greater than 2 kHz. However, at lower spinning rates small satellite-like peaks become apparent, indicating an AB-type system with $^2J(^{31}P,^{31}P) \approx 380$ Hz. A comparison of the chemical shift tensor with that of the free DBP ligand reveals no dramatic changes in the chemical shift anisotropy upon coordination. The values obtained for δ_{33} here are comparable to those found in the literature for other nickel complexes, primarily five-membered chelate complexes, −20 to −50 ppm,[53] and suggest that the direction of δ_{33} corresponds to the direction of the Ni−P bond.

(b) Complexes of Palladium. The ^{31}P CP/MAS NMR spectrum of *trans*-$(DBP)_2PdCl_2$ exhibits spinning-rate-dependent line shapes typical of so-called "unusual" AB-type spectra.[54] Such phenomena were recently reported for some similar trans complexes of palladium and platinum.[55] At spinning rates greater than 1.5 kHz, one peak symmetrically flanked by small peaks is observed, the relative intensities of which are higher in the spinning sidebands than in the center multiplet. At spinning rates below 1.5 kHz, the center peak splits and the outer peaks increase in relative intensity while the total width of the multiplet decreases. Such unusual AB-type spectra generally arise from pairs of crystallographically equivalent but magnetically nonequivalent spins. In contrast to those for the AB multiplets observed in solution NMR, the $^2J(^{31}P,^{31}P)$ coupling constant is given by the separation between alternate peaks in "unusual" AB patterns in solid-state NMR spectra. The value of $^2J(^{31}P,^{31}P)$ determined for *trans*-$(DBP)_2PdCl_2$ is 530 Hz, indeed indicative of a trans arrangement of the phosphine ligands. In principle, the analysis of the stationary powder pattern requires theoretical treatment as an AB spin system and depends on the orientations of the chemical shift tensors relative to the homonuclear spin−spin interactions. However, the static powder pattern observed for *trans*-$(DBP)_2PdCl_2$ exhibits too few features to permit such an exact analysis. Because the spin−spin coupling interactions are small compared to differences between the various principal components of the shift tensor, the spin−spin interactions were neglected. Consequently, errors in the principal components of the CS tensor are somewhat larger (±10 ppm). For *trans*-$(DBP)_2PdBr_2$, essentially the same spectrum type was observed, but less well resolved. Apparently, substitution of Br for Cl has no significant effect on the phosphorus chemical shift anisotropy. The sample of $(DBP)_2PdI_2$ studied here is a mixture of cis and trans isomers. The effect of substituting I for Cl on the phosphorus chemical shift anisotropy is more pronounced and a significant increase in shielding is observed along the direction corresponding to δ_{33}. There is also a clear difference in the chemical shift anisotropies of the cis and trans isomers of $(DBP)_2PdI_2$. In contrast, the cis and trans isomers of $(DMPP)_2PdBr_2$ show only minor differences in their phosphorus chemical shift tensors.[56]

(c) Complexes of Platinum. Platinum contains 33.8% of the spin $^1/_2$ isotope ^{195}Pt. Therefore, the ^{31}P CP/MAS spectra

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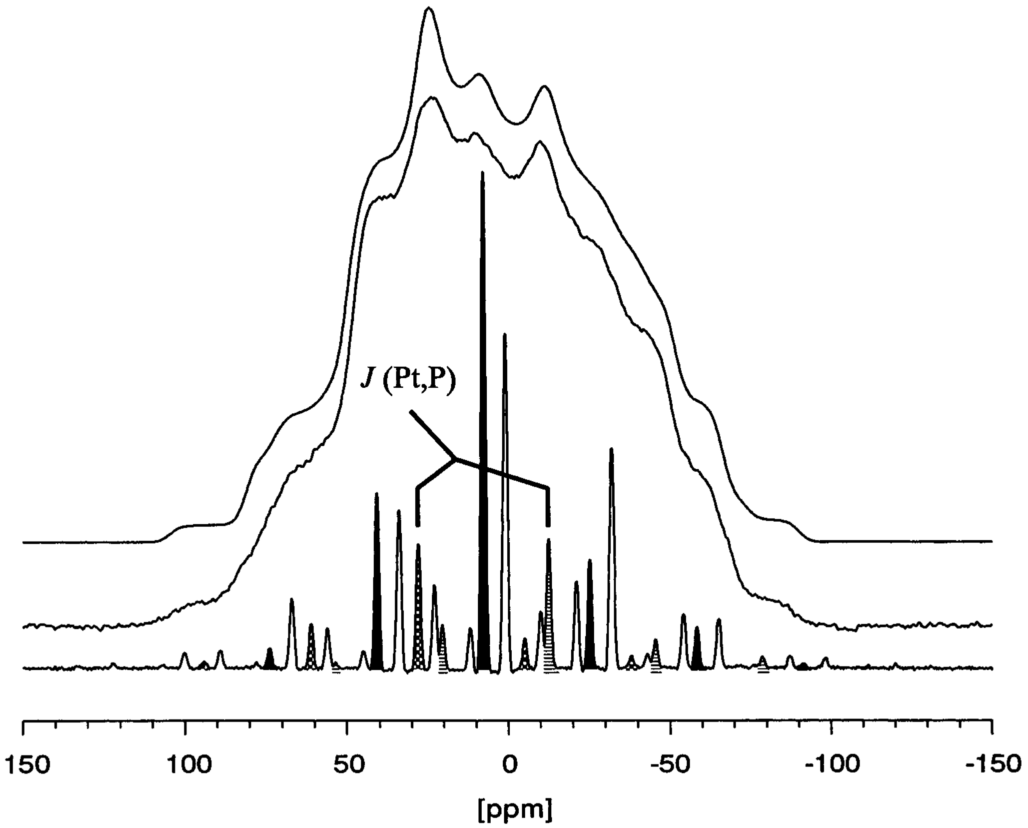

Figure 6. ^{31}P NMR spectra of powder samples of *cis*-$(DBP)_2PtCl_2$. Top trace: spectrum calculated for the stationary sample using the values given in Table 3. Middle trace: experimental spectrum for the stationary sample, 1548 scans, 40 s recycle delay. Bottom trace: MAS spectrum at 2675 Hz, 520 scans. For one of the two phosphorus sites, the uncoupled center peak and associated spinning sidebands are shaded dark, while the associated ^{195}Pt satellite peaks are hatched.

of the platinum complexes investigated here contain an isotropic peak due to phosphorus bonded to NMR inactive platinum isotopes, flanked by ^{195}Pt satellites. Phosphorus spectra of *cis*-$(DBP)_2PtCl_2$ are shown in Figure 6. For each of the complexes $(DBP)_2PtX_2$ (X = Cl, Br, I) the cis complex was obtained, as indicated by the values of $^{1}J(^{195}Pt,^{31}P)$.[41,42] As well, two sites were observed in the ^{31}P CP/MAS NMR spectra of each complex. As in the case of Pd, the chloro and bromo derivatives yield similar spectra, except for the line widths, while the iodo compound differs. In order to calculate the theoretical line shape resulting from stationary samples, the ^{31}P CP/MAS spectra obtained under conditions of slow spinning were analyzed first. The parameters obtained from these spectra were then refined using the spectra of the stationary sample. The line shapes of the satellites in the spectra of spinning and stationary samples are dependent upon the indirect and direct $^{195}Pt-^{31}P$ spin–spin coupling tensors and their relative orientations to the phosphorus chemical shift tensor, while the line shape of the central peak depends solely on the phosphorus chemical shift tensor; the analysis of such spectra of platinum phosphine complexes has been described.[41,42] In the present case, best agreement between calculated and experimental spectra was obtained by using the chemical shift anisotropy values reported in Table 3 and values of 2.0 ± 0.5 kHz for the anisotropy in the indirect $^{195}Pt-^{31}P$ spin–spin coupling tensor together with an orientation where δ_{22} is parallel to the Pt–P bond; these results are in agreement with other studies on phosphine complexes of platinum.[41,42] For all compounds, both sites have clearly different values of $^{1}J(^{195}Pt,^{31}P)$, and it seems that the greater value of $^{1}J(^{195}Pt,^{31}P)$ is associated with a higher shielding along the direction of δ_{22}. For example, three sites have been observed for *cis*-$(PPh_3)_2PtCl_2$, with $^{1}J(^{195}Pt,^{31}P)$ of 3596, 3727, and 3910 Hz, associated with values of δ_{22} of 3, −10, and −18 ppm, respectively.[41] The two sites of *cis*-$(DBP)_2PtCl_2$ have slightly different Pt–P distances, with greater differences in the Pt–P–C angles.[57] The apparent correlation between δ_{22} and $^{1}J(^{195}Pt,^{31}P)$ may prove useful in assigning the peaks to specific crystallographic sites, as an empirical correlation between $^{1}J(^{195}Pt,^{31}P)$ and the Pt–P separation has long been established.[1,58]

Conclusions

The comparison of the phosphorus chemical shift data obtained for DBP and its derivatives with those of other phosphines illustrates that it has characteristics similar to those of triphenylphosphine; however, the asymmetric tensors for DBP reflect reduced local symmetry at the phosphorus site of this ligand. From data obtained here and those reported in the literature,[3] it appears that each class of compounds—phosphines, phosphine chalcogenides, and phosphine transition metal complexes—exhibits characteristic and unique dependencies of the individual components on changes in the substituents at phosphorus or the coordination partner. For example, in tertiary phosphines, the direction along the approximate C_3 axis is less sensitive to substituent changes than the direction perpendicular to the axis: $\delta_{\parallel}$ ranges from −68 ppm (PMe_3) to −30 ppm (PCy_3), while $\delta_{\perp}$ changes from −61 ppm (PMe_3) to 35 ppm (PCy_3). This trend is quite different in the phosphine oxides: all tertiary phosphine oxides have similar phosphorus chemical shift tensors. Only if the scope is widened to include the halides, does a trend opposite to the one observed for the phosphines become apparent: the chemical shift along the molecular axis

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changes from −311 ppm ($Br_3P{=}O$) to −65 ppm ($Et_3P{=}O$), while $\delta_\perp$ varies to a lesser extent between 12 ppm ($Br_3P{=}O$) and 125 ppm (DBP═O). Moreover, the phosphorus chemical shift tensors in the oxides, sulfides, and selenides do not change in a manner which could be easily related to the popular arguments of changes in electronegativity and/or "π-occupation numbers".

For the complexes of DBP with the group 6 transition metal carbonyls, the component of the phosphorus chemical shift tensor close to the M−P bond has been shown to be relatively independent of the metal and, in fact, has a chemical shift similar to the value observed for the free ligand in the analogous direction. This indicates that the rationalization frequently stated in the literature, that in phosphines the direction of the highest shielding is in the direction of the lone pair because in this direction is the highest electron density, is based on a misconception. Were this the case, one should expect this direction to show the greatest change upon coordination. Besides, no theoretical justification for this explanation is available. The directions which do show a clear dependence upon the metal are the directions perpendicular to the M−P bond. Thus, it is these latter components that are responsible for the characteristic coordination shifts of these complexes.

Group 10 metal complexes, $(DBP)_2MX_2$, have also been investigated. While the bromo complexes appear to show phosphorus chemical shift tensors very similar to those of the chloro complexes, those of the iodo complexes are distinctly different. For the DBP complexes of group 10 metals, there is no evidence for a systematic dependence of the principal components perpendicular to the M−P bond on the nature of the metal, as observed for the group 6 complexes.

From the results presented, it is apparent that numerous parameters affect phosphorus chemical shifts and that we are still far from understanding phosphorus chemical shifts. Although a detailed interpretation of the data presented here will have to await further advances in quantum chemistry calculations, it is clear that systematic experimental studies of the type reported in this paper will play an important role in testing future calculations. The establishment of benchmarks for a series of structurally well-characterized compounds is of paramount importance in testing any theoretical procedure.

While this paper was in press, a theoretical study of phosphorus chemical shift tensors in $M(CO)_5L$ (M = Cr, Mo, W; L = PH_3, etc.) complexes appeared.[59]

Acknowledgment. We wish to thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial assistance in the form of equipment and operating grants (R.E.W.). J.H.N. thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. Discussions with Professor D. B. Chesnut concerning his shielding calculations on phospholes are greatly appreciated. We thank Dr. M. D. Lumsden and Mr. Scott Kroeker for helpful comments. All solid-state spectra were recorded at the Atlantic Region Magnetic Resonance Centre, which is also supported by NSERC.

IC960095Z

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