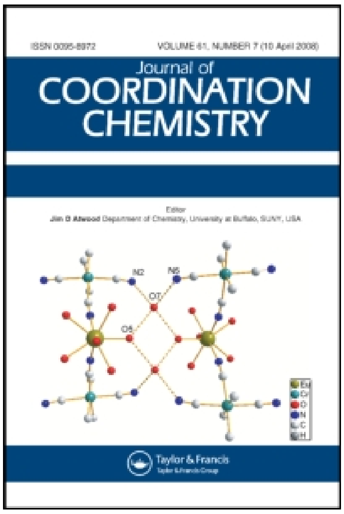

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PHOSPHORUS-31 MAGNETIC RESONANCE STUDIES OF SOME TERTIARY PHOSPHINE OXIDE COORDINATION COMPOUNDS

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Ten new coordination compounds of the type [$Ph_2P(O)CH_2P(O)Ph_2$ [MX_2, where MX_2 = $ZnCl_2$, $CdCl_2$, $CdBr_2$, CdI_2, $HgCl_2$, $HgBr_2$, HgI_2, $CoCl_2$, $CuCl_2$, and $(CH_3)_2SnCl_2$ are reported. Results of phosphorus-31 nmr studies on these and other monodentate tertiary phosphine oxide complexes are discussed. At ambient temperatures, ligand exchange in solution is rapid for these complexes on the nmr time scale, but dissociation of the bidentate ligand appears to be very slight. Some pmr and infrared data are also presented.

INTRODUCTION

Pickard and Kenyon reported the synthesis of some monodentate organophosphine oxide metal complexes in 1906[1]. In the intervening years recently, considerably more has been reported regarding the isolation and characterization of coordination compounds containing these ligands[2–17]. Some bidentate chelating organophosphine oxide complexes are known, primarily with $Ph_2P(O)CH_2P(O)Ph_2$ and alkali or alkaline earth cations[18–20], Co(II), Ni(II), and Cu(II) halides[21–25]. Also some n-$Bu_2P(O)$–$CH_2P(O)n$-Bu_2[26] and $Ph_2P(O)CH_2CH_2P(O)Ph_2$[27] complexes have been described. Use of phosphorus-31 nmr spectroscopy to study phosphoryl coordination compounds has been limited to the determination of the coordination bonding sites of ATP and ADP to metal ions in aqueous solution[28-30], a few solvent extraction studies[31–33], and some anionic chelating phosphoryl esters[34], and bridging complexes.[35] Recently we have reported phosphorus-31 nmr studies of complexes of diphenylphosphinodiphenylphosphorylalkanes[36] and diorganophosphoryl acetic acids.[37]

In a continuation of the studies of phosphoryl coordination complexes and the utility of ^{31}P nmr for use in examining these compounds, we now report the synthesis of several new coordination compounds of bis(diphenylphosphoryl)methane, and the ^{31}P nmr and infrared data for these compounds and some monodentate tertiary phosphine oxide complexes.

EXPERIMENTAL

Phosphorus-31 nmr spectra were recorded on a Varian Associates DP-60 spectrometer operating at 24.3 MHz as previously described[38]. Spectra for the mercury complexes were also recorded on a Brüker HFX-90 spectrometer as previously described[36].

Proton magnetic resonance spectra were recorded on a Varian Associates A60-A spectrometer in $CDCl_3$ or DMSO-d_6 with TMS as an internal standard.

Microanalyses were performed by Dr. Franz Kasler of the University of Maryland.

Melting points were obtained with a Mel-Temp melting point apparatus and are reported uncorrected.

Triphenylphosphine and tributylphosphine oxide were purchased from M and T Chemical Co. The method of Issleib and Müller[39] was used to prepare $(Ph_2P)_2CH_2$. $[Bu_3P{=}O]_4Zn(ClO_4)_2$ was prepared by the method of Karayannis, *et al.*[40] $[Ph_3P{=}O]_2HgBr_2$ was prepared by the method of Frazer, *et al.*[13] All compounds were dried at room temperature and 0.2 mm.

$[Ph_2P(O)]_2CH_2$

Tetraphenyldiphosphinomethane (25.0 g, 0.065 mole) was placed with 600 ml acetone in a 1-liter Erlenmeyer flask. Hydrogen peroxide (30%, 16.2 g, 0.142 mole) was added to 30 ml of distilled water. While the solution was stirred magnetically, the H_2O_2 solution was added with a medicine dropper at a rate sufficient to keep the solution warm. The resulting solution was stirred for a half hour, the solvents almost completely removed by rotary evaporation

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and 500 ml hexane added. The solid product, 98% yield, was removed by filtration. This ligand was used without further purification in the preparation of the complexes, but a 1 g sample was recrystallized from xylene for analysis and spectral data. Triphenylphosphine oxide was similarly prepared.

$[Ph_2P(O)CH_2P(O)Ph_2]ZnCl_2$

Zinc chloride (0.33 g, 2.4 mmol) was dissolved in 20 ml hot $CH(OEt)_3$. One gram of the ligand (2.4 mmol) was added. The solution was heated and stirred magnetically for 30 minutes. The resultant white solid was removed by filtration, washed with EtOH, and dried. Similarly prepared was $[Ph_2P(O)CH_2P(O)Ph_2]HgBr_2$ (refluxed 8 hours).

$[Ph_2P(O)CH_2P(O)Ph_2]CdCl_2$

One gram of the ligand (2.4 mmol) was dissolved in refluxing $CH(OEt)_3$. The flask was transferred to an oil bath (60°) and $CdCl_2 \cdot 2\frac{1}{2}H_2O$ (0.54 g, 2.4 mmol) was added. The solution was heated and stirred magnetically for two hours. The solids were removed by filtration, treated with a large volume of hot $CHCl_3$ and refiltered while hot. The volume of $CHCl_3$ was slowly reduced to 10 ml with a stream of nitrogen, causing the compound to separate as white crystals. These were removed by filtration, washed with EtOH and dried.

$[Ph_2P(O)CH_2P(O)Ph_2]CdBr_2$

One gram of the ligand (2.4 mmol) and 0.83 g of $CdBr_2 \cdot 4H_2O$ (2.4 mmol) were each dissolved separately in 30 ml hot EtOH. The solutions were combined in a 100 ml round bottom flask and refluxed for a half hour. The white solid was removed by filtration, washed with 15 ml EtOH, and dried.

$[Ph_2P(O)CH_2P(O)Ph_2]CdI_2$

One gram of the ligand (2.4 mmol) and 0.88 g CdI_2 (2.4 mmol) were dissolved separately in 30 ml hot acetone, combined in a 100 ml round bottom flask and refluxed for six hours. The volume was reduced to about 5 ml with a rotary evaporator. Slow addition of 10 ml xylene resulted in crystallization of the compound. The crystals were removed by filtration, washed with EtOH, and dried. Similarly prepared were $[Ph_2P(O)CH_2P(O)Ph_2]HgCl_2$ and $[Ph_2P(O)CH_2P(O)Ph_2]HgI_2$.

$[Ph_2P(O)CH_2P(O)Ph_2]CuCl_2$

One gram of the ligand (2.4 mmol) was dissolved in 30 ml of EtOH, and $CuCl_2 \cdot 2H_2O$ (2.4 mmol) added. The solution was warmed on a steam bath until the volume was reduced to *ca.* 10 ml. The complex was removed by filtration, washed with a little EtOH and dried. Similarly prepared was $[Ph_2P(O)CH_2P(O)Ph_2]CoCl_2$.

$[Ph_2P(O)CH_2P(O)Ph_2]Sn(CH_3)_2Cl_2$

One gram of the ligand (2.4 mmol) and 0.53 g $(CH_3)_2SnCl_2$ (2.4 mmol) were dissolved separately in 50 ml hot benzene. The solutions were combined and the mixture allowed to digest for 30 minutes on a steam bath. The solution was allowed to stand overnight and filtered. The solid was recrystallized from MeOH.

The analytical and physical data appear in Table I.

TABLE I

Analytical and physical data for $Ph_2P(O)CH_2P(O)Ph_2$ complexes

	Carbon		Hydrogen		Other (element)		MP	Color	% Yield
	Calcd	Found	Calcd	Found	Calcd	Found			
$Ph_2P(O)CH_2P(O)Ph_2$	72.11	72.03	5.33	5.37	–	–	178–9	white	98
$[Ph_2P(O)CH_2P(O)Ph_2]ZnCl_2$	54.33	54.05	4.01	4.01	12.38(Cl)	12.74(Cl)	288–90	white	83
$[Ph_2P(O)CH_2P(O)Ph_2]CdCl_2$	50.07	50.35	3.70	3.91	11.83(Cl)	12.06(Cl)	292–95	white	49
$[Ph_2P(O)CH_2P(O)Ph_2]CdBr_2$	43.60	43.61	3.22	3.12	23.2(Br)	23.4(Br)	291–94	white	73
$[Ph_2P(O)CH_2P(O)Ph_2]CdI_2$	38.36	38.40	2.83	3.01	32.4(I)	32.2(I)	287–91	lt. yel.	94
$[Ph_2P(O)CH_2P(O)Ph_2]CuCl_2$	54.50	55.06	4.03	4.08	–	–	133–35	brown	49
$[Ph_2P(O)CH_2P(O)Ph_2]CoCl_2$	54.99	56.51	4.06	4.10	–	–	140–50d	blue	83
$[Ph_2P(O)CH_2P(O)Ph_2]HgCl_2$	43.64	43.72	3.22	3.18	9.01(P)	9.15(P)	139–41d	white	91
$[Ph_2P(O)CH_2P(O)Ph_2]HgBr_2$	38.65	38.35	2.86	2.99	7.98(P)	7.86(P)	145–47	white	67
$[Ph_2P(O)CH_2P(O)Ph_2]HgI_2$	34.48	34.84	2.55	2.60	7.12(P)	7.07(P)	188–90	lt. yel.	43
$[Ph_2P(O)CH_2P(O)Ph_2](CH_3)_2SnCl_2$	50.98	50.54	4.44	4.52	11.15(Cl)	10.51(Cl)	218–20	white	70

d = decompose

TABLE II

Phosphorus-31 NMR data for phosphine oxide complexes

Compound	δ_P^a	Δ	Solvent
$Ph_2P(O)CH_2P(O)Ph_2$	−24.2(.2)	----	CH_2Cl_2
$Ph_2P(O)CH_2P(O)Ph_2$	−23.8(.2)	----	DMSO
$[Ph_2P(O)CH_2P(O)Ph_2]ZnCl_2$	−29.2(.4)	−5.4	DMSO
$[Ph_2P(O)CH_2P(O)Ph_2]CdCl_2$	−28.8(.2)	−5.0	DMSO
$[Ph_2P(O)CH_2P(O)Ph_2]CdBr_2$	−29.8(.2)	−6.0	DMSO
$[Ph_2P(O)CH_2P(O)Ph_2]CdI_2$	−30.0(.2)	−6.5	DMSO
$[Ph_2P(O)CH_2P(O)Ph_2]HgCl_2$	−28.7[b]	−4.5	CH_2Cl_2
$[Ph_2P(O)CH_2P(O)Ph_2]HgBr_2$	−28.4[b]	−4.2	CH_2Cl_2
$[Ph_2P(O)CH_2P(O)Ph_2]HgI_2$	−26.7[b]	−2.5	CH_2Cl_2
$[Ph_2P(O)CH_2P(O)Ph_2](CH_3)_2SnCl_2$	−30.5(.2)	−5.5	$CHCl_2CN$
$[(Bu_3P{=}O)_4Zn](ClO_4)_2$	−68.7[c]	−25.7	CH_2Cl_2
$(Ph_3P{=}O)_2HgBr_2$	−30.8[d]	−5.8	CH_2Cl_2

[a] ppm relative to 85% H_3PO_4. Negative numbers are downfield from H_3PO_4. Values in parentheses are standard deviations.

[b] Spectra recorded by C. A. Tolman.

[c] δ $Bu_3P{=}O = -43.0$.

[d] δ $Ph_3P{=}O = -25.0$

RESULTS AND DISCUSSION.

Simple coordination compounds of bis-diphenylphosphorylmethane, $Ph_2P(O)CH_2P(O)Ph_2$, with $ZnCl_2$, $CdCl_2$, $CdBr_2$, CdI_2, $HgCl_2$, $HgBr_2$, HgI_2, $CuCl_2$, $CoCl_2$, and $(CH_3)SnCl_2$ have been prepared and characterized. Phosphorus-31 nmr data of these and two monodentate phosphine complexes, $[(n\text{-}Bu_3PO)_4Zn](ClO_4)_2$ and $(Ph_3PO)_2HgBr_2$, are recorded in Tables II and III. All of the complexes demonstrate a downfield chemical coordination shift (defined as $\delta_{complex} - \delta_{ligand}$). This can be explained as simply a deshielding of the phosphorus atom effected by the donation of phosphoryl oxygen electrons to the metal. The very large negative chemical coordination shift of $[(Bu_3P{=}O)_4Zn](ClO_4)_2$ could be a reflection of the stronger Lewis acid properties of a Zn^{++} ion versus the $ZnCl_2$ moiety, causing a large deshielding of the phosphoryl group.

Several other points should be noted from the

TABLE III

^{31}P chemical shifts of complexes with excess ligand

Compound	Moles (moles of P) x 10^3	Moles of excess ligand (moles of P) x 10^3	δ(ppm)
$[(Bu_3PO)_4Zn](ClO_4)_2^a$	.492(1.97)	0(0)	−68.7
	.492(1.97)	1.05(1.05)	−62.8
	.492(1.97)	1.42(1.42)	−60.9
	.492(1.97)	2.84(2.84)	−57.5
	.492(1.97)	3.80(3.80)	−55.2
	.492(1.97)	6.65(6.65)	−51.6
	0(0)	ligand in CH_2Cl_2	−43.0
$[Ph_2P(O)CH_2P(O)Ph_2]ZnCl_2^b$	.565(1.13)	0(0)	−29.2
	.565(1.13)	.104(.208)	−27.4
	.565(1.13)	.213(.427)	−27.2
	.565(1.13)	.335(.669)	−27.1
	.565(1.13)	.461(.923)	−26.8
	.565(1.13)	.591(1.18)	−26.7
	.565(1.13)	.750(1.50)	−26.1
	.565(1.13)	1.05 (2.10)	−25.5
	0(0)	ligand in DMSO	−23.8

[a] in CH_2Cl_2

[b] in dimethyl sulfoxide

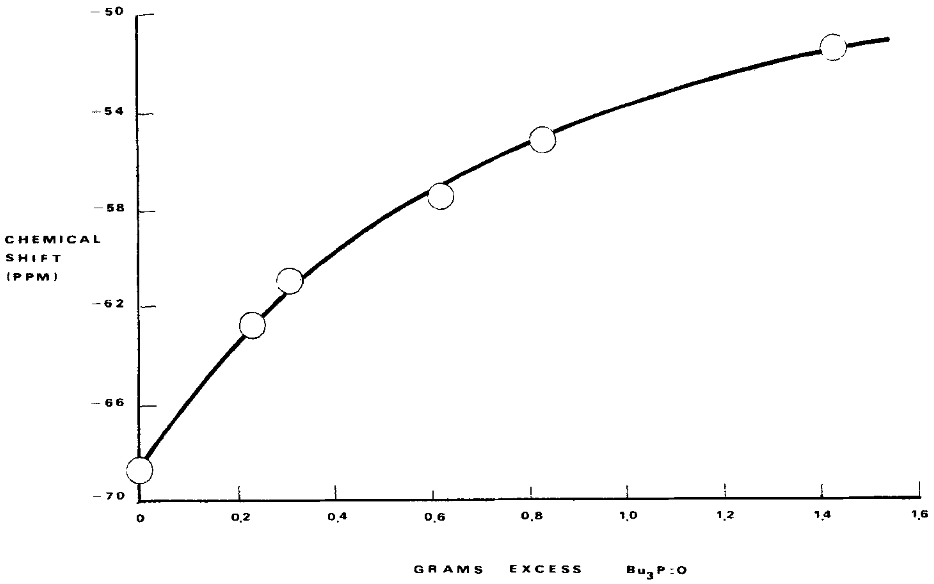


FIGURE 1 Change in ^{31}P chemical shift of [$(Bu_3PO)_4Zn$]$(ClO_4)_2$ with excess ligand.

phosphorus-31 nmr data. First, ligand exchange is rapid on the nmr time scale for both the monodentate ligand complex, [$(Bu_3PO)_4Zn$]$(ClO_4)_2$, and the bidentate complex, ($Ph_2P(O)CH_2P(O)Ph_2$)$ZnCl_2$. This is shown by the data in Table III. Only one peak is evident when excess ligand is added to the complex in solution. The chemical shift of the single peak moves upfield, nearer the chemical shift of the pure ligand, as the concentration of the excess ligand increases (Figure 1). In the case of [$Ph_2P(O)CH_2P(O)Ph_2$]$ZnCl_2$, calculation of the expected chemical shift of the 'complexed ligand' from the weighted average of free ligand and complex and assuming the dissociation constant of the complex is very small (*i.e.*, the amount of free ligand arising from complex dissociation is negligible with respect to the excess free ligand), gives calculated values (−28.0, −28.5, −29.1, −29.3, −29.8, −29.1, −28.5; average, −28.9) very close to the experimental chemical shift of −29.2 ppm. This corroborates the assumption that the dissociation constant is very small for the complex of the chelated phosphine oxide ligand and that the chemical shift observed for a solution of the pure complex is essentially the chemical shift of the complexed ligand or at most, a weighted average of free and complexed ligand that is almost entirely in complexed form. The same is not true for [$(n\text{-}Bu_3PO)_4Zn$]$(ClO_4)_2$. In this case the same calculation gives results which indicate a substantial dissociation of the monodentate phosphine oxide ligand. For example, assuming negligible dissociation of the complex when excess ligand is present gives the calculated chemical shift of the "complexed ligand" as −80 ppm whereas the chemical shift of a solution of the pure complex is −68.7 ppm. The free ligand has a chemical shift of −43 ppm. No calculations were attempted to determine the degree of dissociation because of the numerous stepwise dissociation reactions involved and the lack of knowledge of the chemical shifts of the complexes in the intermediate species, *e.g.*, L_3Zn^{++}, L_2Zn^{++}, etc.

Second, although cadmium, mercury, and tin all have isotopes with nuclear spins of ½(^{111}Cd, 12.8% abundance; ^{113}Cd, 12.3% abundance; ^{199}Hg, 16.8% abundance; ^{117}Sn, 7.6% abundance; ^{119}Sn, 8.6% abundance), no $^2J_{POM}$ coupling is observed at room temperature, although one example of such long-range coupling is known[41] and a few other examples of long-range J_{PM} couplings have been reported[42,43]. The lack of observable $^2J_{POM}$ could be attributed to either ligand exchange or to a negligably small $^2J_{POM}$, probably the former.

Third, assuming the chemical shifts of solutions of the complexes are indeed the chemical shifts of the complexed ligands in the cases of the bidentate phosphine oxides, as indicated by the above studies, there appears to be a correlation between the 'hardness' of the metal center and the coordination chemical shift of the ligand. For example, the absolute value of the coordination chemical shift increases in the order $HgCl_2 < CdCl_2 < ZnCl_2$ and also in the order $HgI_2 < HgBr_2 < HgCl_2$. However, the cadmium halides are in the reverse order. Considering (a) that the assumption of only slight dissociation of the complexes was not proven for each compound, (b) the necessity of using different solvents because of different solubility characteristics, and (c) the fact that the coordination chemical shift differences are quite small, an unequivocal statement regarding hardness of the metal center and coordination shift cannot be made from these data. There is, however, some evidence for the trend.

Fourth, no ^{31}P signals were observed for the Cu(II) and Co(II) complexes because of their paramagnetism[28,44]

And finally, the six coordinate complex, $[Ph_2P(O)CH_2P(O)Ph_2]Me_2SnCl_2$, exhibits only one ^{31}P nmr peak. However, because of the labile phosphine oxide ligand behavior, this lends no information on the stereochemistry of the compound.

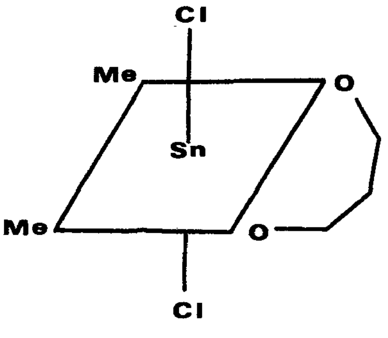
Proton magnetic resonance is more valuable in this respect. The pmr spectrum of $[Ph_2P(O)CH_2P(O)Ph_2](CH_3)_2SnCl_2$ consists of the following peaks: aromatic (δ = 7.2 – 7.9, 20H), methylene (δ = 3.69, J_{PH} = 13.8H, 2H), methyl (δ = 1.20, 6H, $J_{^{119}Sn\text{-}H}$ = 90.5 Hz, $J_{^{117}Sn\text{-}H}$ =

TABLE IV
Infrared data of $Ph_2P(O)CH_2P(O)Ph_2$ Compounds

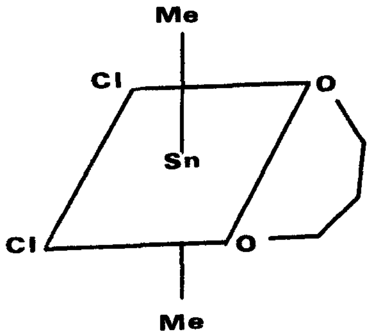
Compound	$\nu^a_{P=O}$	$\Delta\nu^a_{P=O}$	Other Bands[a]
$Ph_2P(O)CH_2P(O)Ph_2$	1195	–	3000 (b), 2850 (w), 2190 (w), 1560 (w), 1460 (w), 1420 (w), 1350 (w), 1155 (sh), 1116 (s), 1104 (sh), 1024 (w), 990 (w), 797 (s), 779 (s), 740 (s), 726 (s), 613 (w), 552 (m), 517 (m), 501 (s), 466 (m), 431 (w)
$[Ph_2P(O)CH_2P(O)Ph_2]ZnCl_2$	1158d	−37	1586 (w), 1476 (w), 1433 (m), 1123 (m), 1095 (w), 996 (w), 787 (s), 740 (m), 687 (s), 574 (m), 502 (s)
$[Ph_2P(O)CH_2P(O)Ph_2]CdCl_2$	1161	−34	3050 (b), 1593 (w), 1485 (w), 1440 (s), 1350 (w), 1123 (m), 1098 (sh), 1071 (w), 1026 (w), 997 (w), 784 (s), 750 (sh), 741 (s), 731 (m), 691 (s), 675 (sh), 616 (w), 569 (m), 518 (sh), 505 (s)
$[Ph_2P(O)CH_2P(O)Ph_2]CdBr_2$	1159	−36	3055 (m), 2927 (w), 2870 (w), 1610 (w), 1582 (m), 1475 (m), 1425 (s), 1345 (m), 1320 (w), 1295 (w), 1123 (s), 1100 (m), 1070 (m), 1027 (w), 997 (m), 923 (w), 848 (w), 787 (s), 742 (s), 731 (s), 691 (s), 676 (sh), 569 (m), 517 (sh), 505 (s)
$[Ph_2P(O)CH_2P(O)Ph_2]CdI_2$	1161	−34	1686 (w), 1588 (w), 1477 (m), 1350 (w), 1221 (w), 1124 (m), 1095 (sh), 1070 (w), 1024 (w), 997 (w), 782 (s), 740 (s), 690 (s), 569 (m), 505 (s)
$[Ph_2P(O)CH_2P(O)Ph_2]CuCl_2$	1152	−43	3055 (w), 2940 (w), 2880 (w), 1581 (w), 1475 (w), 1426 (m), 1341 (w), 1020 (s), 1094 (s), 1058 (m), 1025 (w), 994 (w), 924 (b), 895 (w), 780 (s), 748 (s), 687 (s), 566 (w), 515 (sh), 501 (s)
$[Ph_2P(O)CH_2P(O)Ph_2]HgCl_2$	1166d	−29	3052 (w), 1576 (w), 1471 (w), 1423 (w), 1117 (s), 1096 (m), 1066 (w), 1024 (w), 994 (w), 923 (w), 777 (s), 748 (sh), 739 (s), 715 (sh), 689 (s), 561 (m), 501 (s)
$[Ph_2P(O)CH_2P(O)Ph_2]HgBr_2$	1180	−15	3055 (w), 1685 (m), 1575 (w), 1469 (w), 1424 (m), 1453 (w), 1142 (m), 1119 (m), 995 (w), 775 (s), 764 (sh), 741 (d), 723 (m), 699 (m), 563 (w), 508 (d), 473 (w)
$[Ph_2P(O)CH_2P(O)Ph_2]HgI_2$	1157	−38	1580 (w), 1470 (w), 1435 (m), 1345(w), 1120 (m), 1098 (w), 1079 (w), 1025 (w), 996 (w), 950 (w), 780 (sh), 778 (s), 752 (m), 741 (m), 732 (m), 718 (w), 691 (s), 664 (m), 509 (d), 488 (m), 442 (w), 430 (w)
$[Ph_2P(O)CH_2P(O)Ph_2]Me_2SnCl_2$	1161	−34	3056 (w), 2920 (w), 2880 (w), 1580 (w), 1470 (w), 1430 (m), 1355 (w), 1187 (sh), 1122 (s), 1097 (sh), 1071 (m), 1024 (w), 995 (w), 786 (s), 750 (m), 737 (m), 728 (m), 689 (d), 574 (w), 567 (m), 513 (m), 502 (s), 492 (s)
$[Ph_2P(O)CH_2P(O)Ph_2]NiCl_2$	1168	−27	1580 (w), 1465 (w), 1431 (m), 1350 (w), 1133 (s), 1115 (sh), 1080 (m), 1044 (w), 1013 (w), 994 (w), 974 (s), 743 (s), 697 (s), 571 (m), 501 (s)

[a] In cm^{-1}. b, broad; d, average of a doublet; m, medium; s, strong; sh, shoulder; w, weak.

88.5 Hz). The observation of only one methyl peak indicates that the two methyl groups are equivalent. Thus there are only two reasonable structures for the compound, A and B.



A



B

Mullins[45] demonstrated that $[Ph_3P{=}O]_2Sn(CH_3)_2Cl_2$ is an octahedral complex with the two methyl groups mutually *trans*, the two chlorine atoms mutually *cis*, and each *trans* to a $Ph_3P{=}O$ using Mössbauer and dipole moment data. Earlier Das and Kitching[46] reported that $J_{^{119}Sn\text{-}H}$ is 88 Hz in this complex (they did not report a $J_{^{117}Sn\text{-}H}$ value). Thus, considering the *cis* nature of our phosphine oxide ligand, structure B would appear to be correct. The pmr spectra of the other chelate complexes were essentially identical to that of the free ligand, with an aromatic multiplet at $\delta = 7 - 8.1$ and a triplet for the methylene protons, which are split by the two equivalent phosphorus atoms at $\delta = 3.58 - 3.60$. $^2J_{PCH}$ varies only from 14.1 Hz to 14.4 Hz.

The phosphoryl stretching frequency data appear in Table IV. This band usually appears as the strongest band between 1100 and 1300 cm^{-1}.[47] However, complexation or hydrogen bonding can shift the band to much lower frequencies[4,6–11,13,14,19,21,22,26,27] This effect is generally attributed to a weakening of the phosphoryl bond caused by the donation of electrons from the oxygen atom to the metal atom[4,8] Qualitatively, this is in agreement with the phosphorus-31 nmr data; however, differences are observed when quantitative comparisons are attempted. There are several possible reasons why this could be so. First, infrared spectra were run as KBr pellets while the nmr data were obtained on solutions where ligand exchange is known to occur. Second, the infrared bands are generally broad and not well resolved; indeed, two compounds exhibited doublets. Cotton[8] has attributed these doublets in some monodentate complexes to coupling of the P=O vibrations, or to the existence of non-equivalent ligands in the crystal. Following Cotton's format[8], the phosphoryl values are listed as averages when doublets appeared. And third, instrumental limitations dicate an accuracy of a ±5 cm^{-1} on these data.

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