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An NMR Study of Phenyl- and Diphenylphosphine Alkali Metal Salts

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The ^{1}H, ^{13}C, and ^{31}P NMR spectra were observed for the title salts in several solvents. The formation of the salts by the deprotonation of the neutral precursors causes significant changes in their NMR parameters. First, the delocalization of the excess charges into the phenyl ring of the salts was confirmed from the ^{1}H and ^{13}C chemical-shift data. Second, the parameters concerned with the center of the anions are dependent on the circumstances of the center atom, phosphorus, such as the hybridization. The results are discussed in terms of the effects of the counter cations and the solvents. Third, a strong polar solvent, HMPA, exerts significant effects on the chemical shifts and the one-bond ^{13}C-^{31}P coupling constants. These parameter changes are explained in terms of an equilibrium between two kinds of ion-pairs (contact ion-pairs and solvent-separated ion-pairs). The parameters obtained in this solvent, HMPA, correspond to those of the solvent-separated ion-pairs or the free anions.

The NMR technique is a useful and efficient technique for investigating many aspects of the anionic species of organic compounds in solutions. Among such species, the carbanions are the most investigated species; they have a carbon atom as an anionic center.[1,2] Recently, there have appeared several articles concerned with the anionic species with heteroatoms as anionic centers.[3,4] However, there has not yet been sufficient discussion on the accumulation of enough data about the problems of these anions, such as their structures, electron distributions, bondings, and counter cations.

In this article we wish to report our measurements of the ^{1}H, ^{13}C, and ^{31}P chemical shifts for the anionic species produced from phenyl- and diphenylphosphines, whose sodium salts were reported previously.[3a] The results are discussed in terms of the structures of the anions, solvents, and counter cations, and the temperature.

Experimental

The phenylphosphine and chlorodiphenylphosphine used as starting materials were commercially available and were used without further purification. These starting materials were dried and distilled over calcium hydride, and then degassed and stored in sealed vessels with a break seal.

The tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), and 2-methyltetrahydrofuran (2MTHF) were refluxed and distilled over sodium metal and then stored over sodium-potassium alloy. The hexamethylphosphoric triamide (HMPA) and tetrahydrofuran-d_8 (THF-d_8) were dried and distilled over calcium hydride, and then degassed and stored in sealed vessels with a break seal.

The phenylphosphine was allowed to react with butyllithium in hexane under a vacuum. Then, after all volatile materials had been distilled off in a vacuum, the residue was dissolved in a solvent (THF, DME, 2MTHF, HMPA, or THF-d_8). The solution of the resulting lithium salt was filtered into an NMR tube, which was then sealed under a vacuum.

Diphenylphosphine alkali metal salts were generated from chlorodiphenylphosphine by means of a halogen-metal exchange reaction. The reaction was carried out so that the starting material was in contact with lithium, sodium, or potassium metal flakes in a solvent at room temperature in a reaction vessel under a vacuum. The solution was kept in the vessel with stirring for a day for the reaction to be completed. Then, the resulting solution was filtered into an NMR tube, which was then sealed under a vacuum. All the NMR samples were prepared as approximately 1M solutions sealed in 5- or 10-mm o.d. tubes.

All the NMR spectra were measured on a Varian XL-200 Fourier transform spectrometer at the ambient temperature (ca. 25 °C). The ^{1}H and ^{13}C chemical shifts were referred to the more (or most) shielded peaks of the solvents, and then converted to the values from TMS by taking 1.79 and 26.40 (or 1.75 and 25.40) for δ_H and δ_C of THF(or THF-d_8), and 21.20, 37.00, and 58.80 for δ_C of 2MTHF, HMPA, and DME respectively. The ^{31}P chemical shifts were measured externally relative to a 1 wt% H_3PO_4 solution dissolved in D_2O.

Results and Discussion

^{1}H Chemical Shifts. The ^{1}H chemical-shift data for the compounds measured in THF-d_8 are summarized in Table 1, together with the citation numbers of the compounds. The ^{1}H chemical shifts of the anionic

Table 1. ^{1}H Chemical Shifts of Phenyl- and Diphenylphosphines and Their Anions in ppm[a)]

No.	Compound	P-H	H-2	H-3	H-4
1	$PhPH_2$	3.97	7.51	7.28[b)]	7.28[b)]
1a	PhPHLi	2.13	7.09	6.56	6.27
1b	PhPHNa[c)]	2.23	7.16	6.58	6.29
2	Ph_2PH	5.24	7.51	7.31[b)]	7.31[b)]
2a	Ph_2PLi	—	7.46	6.79	6.50
2b	Ph_2PNa	—	7.53	6.84	6.57
2c	Ph_2PK	—	7.48	6.80	6.48

a) Chemical shifts are measured for ca. 1M (1M=1 mol dm^{-3}) solutions in THF-d_8 relative to the more shielded residual solvent peak, which is taken as 1.75 ppm from TMS. b) The values are not determined precisely because of the signal overlapping. c) The values are cited from Ref. 3a.

compounds from **1a** to **2c** are more shielded than those of the corresponding neutral molecules, **1** and **2**, except that the ortho-proton shifts of the diphenylphosphine alkali metal salts are slightly deshielded. The shift changes of the P-H protons from phenylphosphines to their anionic molecules are ca. 1.7 ppm because of an increased shielding caused by the negative charge on the phosphorus atom. There is a small but significant downfield shift of the P-H proton on going from **1a** to **1b** (0.10 ppm), in accord with a greater charge density in this position in the former species.

The changes in the ^{1}H chemical shifts of the phenyl-ring protons are in the ranges from −0.42 to 0.02, from −0.72 to −0.47, and from −1.01 to −0.83 ppm for the ortho, meta, and para protons respectively. The ring-proton shifts are influenced by various factors. The ortho-proton shift is affected by inductive, resonance, magnetic anisotropy, and electric-field effects from the phosphorus atom as an anionic center. These effects, however, are much smaller for the meta-proton shift, and probably only the resonance effect is important for the para proton shift.[5] This is why the upfield shifts of the para-protons are regarded as a rough estimation of the charge delocalization.

The reason that the ortho-proton shifts have smaller changes than those expected from the resonance effect of the substituent is presumably attributable to some electronic effects caused by the excess charge and the lone-pair electrons on the phosphorus atom.

^{13}C Chemical Shifts. The ^{13}C chemical-shift data for the compounds studied in several solvents are presented in Table 2. The general trends that are apparent in the table are as follows: The formation of the anion species from the corresponding neutral molecules causes the ipso carbon to be significantly deshielded (21 to 42 ppm) and the para carbon to be shielded (9 to 18 ppm), while the ortho and meta carbons show small upfield shifts (2 to 7 ppm).

Table 2. ^{13}C Chemical Shifts of Phenyl- and Diphenylphosphines and Their Alkali Metal Salts in ppm[a)]

No.	Compound	Solvent	C-1	C-2	C-3	C-4
1	$PhPH_2$	THF	129.21	135.33	129.15	128.79
		HMPA	128.34	135.01	129.22	128.82
1a	PhPHLi	2MTHF	158.05	130.27	126.57	117.70
		DME	161.05	130.06	126.87	116.74
		THF	161.63	129.91	126.80	116.53
		HMPA	170.31	127.84	125.50	110.58
1b	PhPHNa[b)]	THF	159.98	130.18	127.15	117.28
2	Ph_2PH	THF-d_8	135.96	134.77	129.28	129.45
		HMPA	135.05	134.27	129.20	129.37
2a	Ph_2PLi	2MTHF	153.92	130.98	127.04	120.11
		THF	157.03	130.55	127.27	119.24
		HMPA	161.45	128.31	126.37	115.70
2b	Ph_2PNa	2MTHF	153.96	130.68	127.44	120.32
		DME	158.29	129.55	127.10	118.21
		THF	156.15	130.55	127.61	119.75
		HMPA	161.71	128.46	126.25	115.53
2c	Ph_2PK	2MTHF	155.02	130.14	127.53	119.78
		DME	159.20	129.02	127.31	117.76
		THF	158.40	129.49	127.76	118.63
		HMPA	161.70	128.50	126.37	115.64

a) Chemical shifts are measured for ca. 1M solutions relative to the more or most shielded peak of the solvent used. See text. b) The values are cited from Ref. 3a.

The ipso-carbon resonances shift clearly towards the downfield direction, contrary to what would be expected from the excess charge delocalization into the phenyl rings, corresponding to a decrease in the electron density at that position. However, such downfield shifts are observed as a general trend for monosubstituted benzenes, in which the substituent is an anionic center, like phenylmethyl carbanions and so on.[3,4,6,7]

The ortho-carbon shifts are affected by various factors because their position is near, second only to the ipso position, to the substituent. However, the ortho- and meta-carbon shifts are indeed of similar magnitudes. This is also a characteristic feature of these anions.[3,4]

It has been considered that para-carbon chemical shifts provide a good measure of charge delocalization, just as para-proton shifts do. It is found that the changes in the para-carbon shifts in the anions produced from **1** and **2** are slightly smaller than those of the phenylmethyl carbanions,[7] but there are significant upfield shifts. Therefore, these upfield shifts show that the degree of charge delocalization into the phenyl ring is relatively large.

^{31}P Chemical Shifts. The ^{31}P NMR data for the compounds studied in several solvents are summarized in Table 3. The trends of the ^{31}P chemical shifts are in agreement with the previously published data.[3a] It is known that the formation of the anions from PH_3 causes the phosphorus atoms to be shielded (16 to 58 ppm).[3a] This is in agreement with the general tendency for the increase in the electron density to result in more shielding on an atom. However, the ^{31}P chemical-shift changes of the anions in Table 3 are in the direction opposite to that expected from the increasing electron density on the phosphorus atoms (5 to 36 ppm downfield shifts).

Batchlor and Birchall have mentioned that the downfield shifts of the phenyl- and diphenylphosphines upon deprotonation might be attributed to a $p\pi$–$p\pi$ interaction between the phenyl ring and the phosphorus atom.[3a] However, such downfield shifts have been observed for the carbons in some carbanions due to the rehybridization of the α-carbon atom.[7] Considering the changes in the ^{31}P–^{13}C coupling constants that will be mentioned later, it seems that the effects of rehybridization (resulting in downfield shifts) and electron density (resulting in upfield shifts) play significant roles in the ^{31}P shifts.

It is found that the solvents with a stronger polarity result in more downfield ^{31}P chemical shifts of the anions as well as more ^{13}C chemical shifts of the

Table 3. ^{31}P Chemical Shifts(ppm) and Coupling Constants(Hz) of Phenyl- and Diphenylphosphines and Their Anions

No.	Compound	Solvent	δ_P	$^1J_{PC}$	$^2J_{PC}$	$^3J_{PC}$	$^1J_{PH}$
1	$PhPH_2$	THF	−125.7	10	15	6	199
		HMPA	−124.1	7	15	6	200
1a	PhPHLi	2MTHF	−114.3	37	14	5	172
		DME	−111.9	44	16	5	162
		THF	−112.6	43	16	4	163
		HMPA	−74.9	59	18	5	144
1b	PhPHNa[a)]	THF	−120.9	44	16	6	162
2	Ph_2PH	THF-d_8	−41.1	11	17	5	216
		HMPA	−40.9	10	17	5	218
2a	Ph_2PLi	2MTHF	−26.2	34	17	6	—
		THF	−20.2	44	18	6	—
		HMPA	5.0	60	20	4	—
2b	Ph_2PNa	2MTHF	−29.2	40	17	6	—
		DME	−12.5	50	20	—	—
		THF	−23.2	45	18	5	—
		HMPA	5.3	63	20	5	—
2c	Ph_2PK	2MTHF	−23.0	44	18	5	—
		DME	−7.6	55	19	5	—
		THF	−10.0	55	18	4	—
		HMPA	5.0	60	20	5	—

a) The values are cited from Ref. 3a.

anions. The ^{31}P chemical shifts of the anions in HMPA are ca.30 to 40 ppm more deshielded than those of the same anions in 2MTHF, whereas the neutral molecules have similar chemical shifts in several solvents.

^{31}P-^{13}C and ^{31}P-^1H Coupling Constants. The phosphorus-carbon and phosphorus-proton coupling constants are summarized in Table 3. It may be pointed out that the values of $^1J_{PC}$ of the anions (34—63 Hz) are significantly larger than those of the neutral molecules (7—12 Hz) and that the solvents with a stronger polarity result in larger values in the $^1J_{PC}$ of the anions. It has been known that the $^1J_{PC}$ are very sensitive to the hybridization of the phosphorus atom and the substituents attached to the atom.[8)] The change in the $^1J_{PC}$ of the anions, therefore, may be attributed to the rehybridization of the phosphorus atom in the anions.

On the other hand, the values of $^2J_{PC}$ and $^3J_{PC}$ of the anions are almost like the values of the neutral molecules. The effects of both the counter cations and the solvents scarcely influence the two- and three-bond phosphorus-carbon coupling constants.

The trend of the change in the one-bond phosphorus-proton coupling constants is in agreement with the previously reported values for sodium salts.[3a)] That is, it is found that the magnitude of $^1J_{PH}$ of the anions (144—172 Hz) is significantly smaller than that of the neutral molecule (ca. 200 Hz). If the signs of the $^1J_{PH}$ are considered to be positive, as has been reported for other systems,[8)] the reduction of the $^1J_{PH}$ in the salts corresponds to a decrease in the s character of the hybridized orbital directed to the hydrogen from the phosphorus atom in the salts as compared with that in **1** or **2**. Further, the increase in the magnitude of the $^1J_{PC}$ in the salts corresponds to the greater conjugation between the p-π orbitals of the two atoms forming the P-C bond as compared with those of the phenylphosphines, **1** and **2**. Additionally, the signs of the $^1J_{PC}$ of several alkylphosphines were noted to be the opposite of those of their phosphonium salts.[8)] Therefore, studies along this line are in progress for several related phosphines and their salts.

It is of interest to point out that the solvents with a stronger polarity result in smaller values of the $^1J_{PH}$ of the anions. The changes in $^1J_{PH}$ are clearly towards the direction opposite to those of $^1J_{PC}$; therefore, the sum of the $^1J_{PH}$ and $^1J_{PC}$ is approximately constant in each species, although the reasons for this are not well understood.

Counter-Cation and Solvent Effects on NMR Parameters. The ^1H chemical shifts of P-H and ortho protons for the phenylphosphine alkali metal salts are slightly affected by the counter cation, but the ring-proton shifts of the anions produced from diphenylphosphines are scarcely affected by the cation, except for the shifts of the sodium salt, which behave differently from the lithium and potassium salts. The counter-cation effects on the carbon and phosphorus chemical shifts are illustrated schematically in Figs. 1 and 2 respectively. According to the variation in the cations from lithium to potassium, the resonance lines of the ipso-carbon and phosphorus atoms move downfield, while the lines of the para-carbons move upfield. However, the ortho and meta carbons scarcely shift at all. These trends can be explained by the fact that carbon and phosphorus chemical shifts show differences, accompanied by changes in the cation size, that reflect the electron-distribution changes in the ion-pairs, like those observed for phenylmethyl carbanions.[6,7] However, the chemical shifts of the ipso carbon and phosphorus atoms of the sodium salts behave curiously, unlike the general expected trend, as is shown in Figs. 1 and 2. For example, the ^{31}P chemical shifts of the sodium salts **2b** are the most shielded among the three salts, **2a—c**. Especially, the characteristic feature of the sodium salts is significant in moderately polar solvents, such as 2MTHF and THF. Therefore, it seems that this phenomenon is connected with an equilibrium between contact ion-pairs and solvent-separated ion-pairs in the anionic solutions. In more polar solvents such as HMPA, therefore, the counter cations do not affect the chemical shifts, because in such solvents the ion-pairs exist only a form of solvent-separated ion-pairs or free ions. It must be noted that the chemical shifts measured in HMPA are quite different from those measured in THF, which is mostly used in carbanion chemistry.[6] Therefore, it is recommended to use HMPA as a solvent for obtaining the chemical-shift values for the solvent-separated ion-pairs in the ion-pair equilibrium. Further, such solvent effects are not observed in the chemical shifts of the neutral molecules, **1** and **2**.

One of the molecular theoretical parameters that gives the degree of solvation consists of Gutmann's donor and acceptor numbers (DN and AN).[9] In view of the concepts of DN and AN, the different behavior of the sodium salts can be explained by saying that, in solvents with a medium DN (20) value, such as 2MTHF and THF, the sodium ion is solvated less than the lithium one because of its smaller AN. Therefore, the sodium salts have an equilibrium with more contact ion-pairs in the ion-pair equilibrium. Therefore, the negative charge is localized more on the anionic-center atom. Therefore, the ^{31}P chemical shifts of **2b** tend to shift towards a more shielded direction than those of the other salts, **2a** and **2c**. Further, the slightly smaller changes in the C_i and C_p chemical shifts of **2b** show that the delocalization of the excess charges into the phenyl ring is less than those of **2a** and **2c**. The solvent effects on the ^{13}C chemical shifts of **1a** are given in Fig. 3. The solvent effects for the shifts of these salts are larger than their counter cation effects. The former effects increase in the order of 2MTHF,DME,THF, and HMPA. As may be seen in Tables 2 and 3, however, the effects for the salts from **2a** to **2c** increase in a slightly different order. The order of DME$\gtrsim$THF> 2MTHF is consistent with that found for the alkali

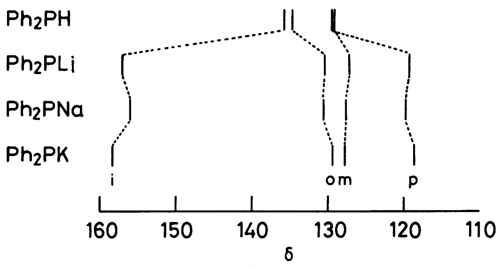

Fig. 1. Schematic diagram of phenyl-^{13}C chemical shifts: Ph=phenyl; i=ipso; o=ortho; m=meta; p=para.

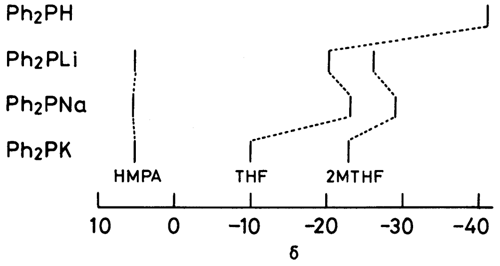

Fig. 2. Schematic diagram of ^{31}P chemical shifts in different solvents and counter cations.

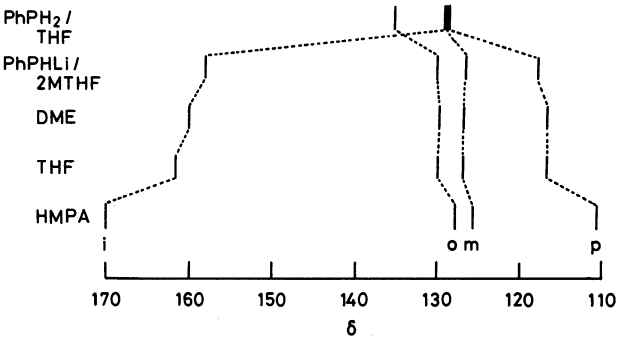

Fig. 3. Schematic diagram of phenyl-^{13}C chemical shifts of **1** and **1a** in four different solvents.

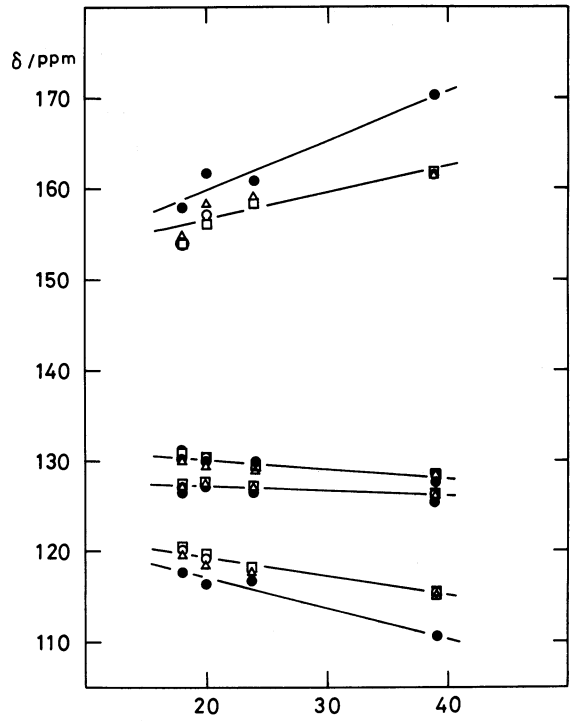

Fig. 4. Plot of phenyl-^{13}C chemical shifts in ppm (ordinate) vs. the DN values of the solvents, which are 18, 20, 24, and 39 for 2MTHF, THF, DME, and HMPA respectively (Ref. 9) (abscissa): **1a**; ●, **2a**; ○, **2b**; □, **2c**; △.

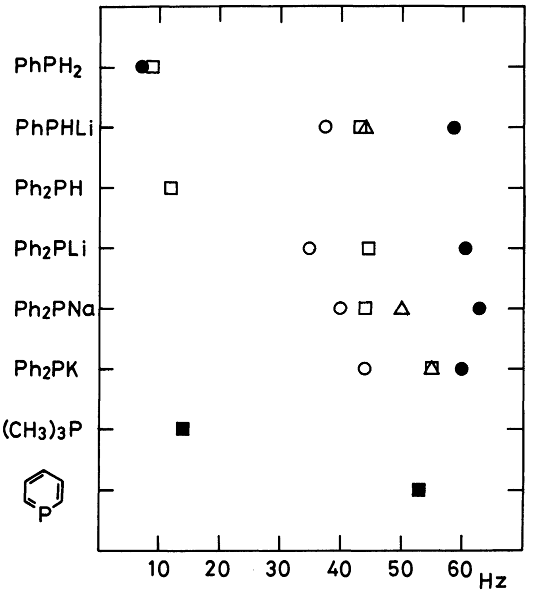

Fig. 5. Schematic diagram of one-bond carbon–phosphorus coupling constants in Hz observed in different solvents: 2MTHF; ○, THF; □, DME; △, HMPA; ●, neat; ■.

metal salts of diphenylmethane.[6] O'Brien et al. stated several reasons for the solvent effects. Their explanation is essentially the same as the concepts of DN and AN. The correlation between such DN and the ^{13}C chemical shifts in several solvents is shown in Fig .4. This shows that the ^{13}C chemical shifts largely reflect the equilibrium between two kinds of ion-pairs. On the other hand, the ^{31}P chemical shifts are not correlated with such DN. This may be because the ^{31}P chemical shifts are not affected by only ion-pair equilibrium, but also by polarization as an anionic center and by rehybridization.

The solvent and counter-cation effects for the $^1J(^{13}C-^{31}P)$ are given in Fig. 5. In the cases of **1** and **2** the coupling constants have a magnitude of about 10 Hz, similar to that of trimethylphosphine. On the other hand, for the alkali metal salts the values tend to increase to a magnitude of about 50 Hz, although their signs were not determined. These values are similar to that of phospharine.[10] The changes in the values are the largest for **2a** (34 to 60) and the least for **2c** (44 to 60 Hz). Further, the effect of the counter cations appears with the largest range in 2MTHF and the least in HMPA. Perhaps the value of 60 Hz is characteristic of the anionic species of **2**. The change in the $^1J_{PC}$ values is affected by the equilibrium between the contact ion-pairs and solvent-separated ion-pairs. The hybridization of the phosphorus atom as an anionic center is similar to that of phospharine.

Recently, two research groups have reported that **2a** exists in a dimeric state in ether at a lower temperature or in a polymeric state in the solid crystal with a covalent bonding between the phosphorus atom and the counter cation.[11,12]

No splitting of the ^{7}Li NMR signal of **2a** was observed in a THF solution in the temperature range from 25 to −110 °C, although the signal moved slightly upfield (0.4 ppm). This may be considered to indicate that the nature of the bonding between phosphorus and lithium atoms of **2a** is essentially ionic or that there exists some other mechanism of signal narrowing in **2a**.

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