then recrystallized from CH_2Cl_2/MeOH to give 0.31 g (64%).

Crystallographic Studies. The crystals of **2**, **7**, and **9** were grown from CH_2Cl_2/hexane at room temperature. General operating procedures and listings of programs were previously given.[1i] Absorption correction was performed on the three compounds (the calculated transmission range is 0.91–0.72 for **2**, 0.92–0.74 for **7**, and 0.94–0.87 for **9**) using ψ scans. Pertinent crystallographic information is summarized in Table IX.

Acknowledgment. We thank the National Science Council, ROC, for a grant to support this research. We also thank Chang-Chuan Chou for the preparation of $(PhHCPz'_2)Mo(CO)_2I_2$ and $(PhHCPz_2)Mo(CO)_3I_2$, Fang-Jy Wu for collecting the X-ray data for **2**, and Professor C. P. Cheng for measuring the magnetic moments.

Registry No. **1**, 120170-13-0; **2**, 120170-14-1; **3**, 120170-15-2; **7**, 125108-55-6; **8**, 124225-84-9; **9**, 125108-63-6; $(H_2CPz_2)W(CO)_3Br_2$, 125108-53-4; $(H_2CPz'_2)W(CO)_3Br_2$, 125108-54-5; $(H_2CPz_2)Mo(CO)_3I_2$, 125108-56-7; $(H_2CPz'_2)Mo(CO)_3I_2$, 125108-57-8; $(H_2CPz''_2)Mo(CO)_3I_2$, 125108-58-9; $(H_2CPz_2)W(CO)_3I_2$, 125108-59-0; $(H_2CPz'_2)W(CO)_3I_2$, 125108-60-3; $(H_2CPz''_2)W(CO)_3I_2$, 125108-61-4; $(PhHCPz_2)Mo(CO)_3I_2$, 125108-62-5; $(H_2CPz'_2)Mo(CO)_4$, 119268-12-1; $(MeCN)_2Mo(CO)_3Br_2$, 105059-20-9; $(H_2CPz_2)Mo(CO)_4$, 119578-37-9; $(H_2CPz_2)W(CO)_4$, 123543-51-1; $(H_2CPz'_2)W(CO)_4$, 119268-13-2; $(H_2CPz''_2)Mo(CO)_4$, 119578-38-0; $(H_2CPz''_2)W(CO)_4$, 125108-64-7; $(PhHCPz_2)Mo(CO)_4$, 125108-65-8; $(PhHCPz'_2)Mo(CO)_4$, 124225-84-9; $(MeCN)_2Mo(CO)_3I_2$, 102349-56-4; $(MeCN)_2W(CO)_3Br_2$, 105059-21-0; $(MeCN)_2W(CO)_3I_2$, 102382-37-6.

Supplementary Material Available: Tables of fractional coordinates of hydrogen atoms and U_{ij} values for non-hydrogen atoms (3 pages); a listing of F_o vs F_c values for **2**, **7**, and **9** (25 pages). Ordering information is given on any current masthead page.

Aspects of the Cleavage of Phosphines with Potassium: Synthesis and Reactivity of Lithium and Potassium Bis(*p*-(dimethylamino)phenyl)phosphide

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The cleavage of the triarylphosphines $P(p\text{-}C_6H_4NMe_2)_3$ and $PhP(p\text{-}C_6H_4NMe_2)_2$ with potassium in ether solvents was found to occur at room temperature. Cleavage of the mixed phosphine $PhP(p\text{-}C_6H_4NMe_2)_2$ was found to give a mixture of products that reflects the relative stability of the phosphides $KP(Ph)(p\text{-}C_6H_4NMe_2)$ and $KP(p\text{-}C_6H_4NMe_2)_2$. Cleavage with lithium resulted in the scrambling of the aryl groups so that the products $LiPPh_2$ and $P(Ph)_2(p\text{-}C_6H_4NMe_2)$ also were obtained. Comparison with the cleavage of PPh_3 shows that $MP(p\text{-}C_6H_4NMe_2)_2$ (M = Li, K) is more nucleophilic than the corresponding phenylphosphide $MPPh_2$. The preparation of the chlorophosphine $ClP(p\text{-}C_6H_4NMe_2)_2$ and its reaction with lithium or potassium is an alternate path to the phosphides. The reaction of $ClP(p\text{-}C_6H_4NMe_2)_2$ with lithium yielded both $LiP(p\text{-}C_6H_4NMe_2)_2$ and $(p\text{-}C_6H_4NMe_2)_2PP(p\text{-}C_6H_4NMe_2)_2$. The amino-substituted potassium phosphide $KP(p\text{-}C_6H_4NMe_2)_2$ is conveniently prepared from $P(p\text{-}C_6H_4NMe_2)_3$ and is a useful intermediate for the synthesis of phosphines that contain amine functional groups.

Introduction

The preparation of water-soluble phosphines for use in aqueous-phase and two-phase catalytic reactions is an area of current interest.[1-7] One goal of two-phase reactions is to achieve catalytic systems in which the products can be easily separated from the homogeneous catalyst. Applications are found in the homogeneous hydrogenation and hydroformylation of olefins. The most successful approach to date is the sulfonation of phenyl groups bonded to phosphorus in tertiary and ditertiary phosphines.[2] For example, sulfonated derivatives of triphenylphosphine[2,3] and of several chiral phosphines such as (*S*,*S*)-2,3-bis(diphenylphosphino)butane[1a] have been reported. Water-soluble phosphines with cationic and neutral polar groups also are of interest.[4-7] Examples of phosphines with quaternary amine functional groups are limited to one such group per phosphorus atom, which limits the water solubility of this type of modified phosphines.[5,7]

Recently we have sought phosphines that contain two or more cationic groups per phosphorus atom for use in aqueous and supported aqueous phase catalysis.[8] The systematic introduction of (dimethylamino)phenyl groups into phosphines and their subsequent quaternization would satisfy this purpose.[9] Tertiary phosphines typically are synthesized by one of two routes, nucleophilic substitution of a chlorophosphine with an organolithium or Grignard reagent or nucleophilic substitution of an alkyl halide or tosylate with a phosphide anion.[10] Furthermore, chlorophosphines may be converted to phosphides through re-

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(1) See for example: (a) Amrani, Y.; Lecomte, L.; Sinou, D.; Bakos, J.; Tóth, I.; Heil, B. *Organometallics* **1989**, *8*, 542. (b) Sinou, D. *Bull. Soc. Chem. Jpn.* **1987**, 480.

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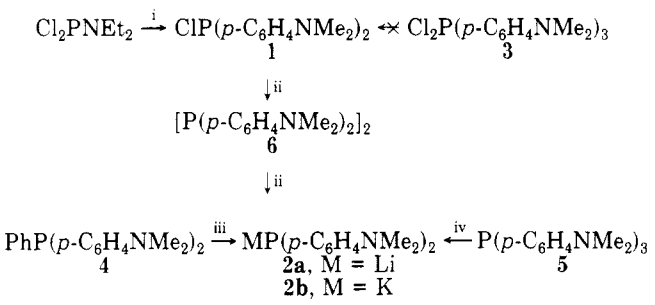
0276-7333/90/2309-0675$02.50/0

Scheme I[a]



[a] Legend: (i) (a) p-$LiC_6H_4NMe_2$, (b) HCl; (ii) Li, THF; (iii) K or Li, THF (yields a mixture of products); (iv) K, THF.

action with alkali metals.[10,11] Thus, two potential precursors to phosphines containing the (dimethylamino)phenyl group are $ClP(p\text{-}C_6H_4NMe_2)_2$ and $[P(p\text{-}C_6H_4NMe_2)_2]^-$ (1 and **2**, respectively). Reference to a route to 1 via the thermal decomposition of $P(p\text{-}C_6H_4NMe_2)_3Cl_2$ (**3**)[12] is made in a review of phosphine synthetic methods.[10] The preparation of the anion **2** is reported in the literature via the cleavage of $PhP(p\text{-}C_6H_4NMe_2)_2$ (**4**) with potassium.[13] This precursor is apparently necessary since the cleavage of $P(p\text{-}C_6H_4NMe_2)_3$ (**5**) is not effected by alkali metals.[13] The basis of this synthetic route stems from the observation that alkali metals generally cleave P–C bonds at the most electron withdrawing alkyl or aryl group.[14] We find, however, that these reactions proceed differently than previously described and, furthermore, that the cleavage of arylphosphines generally is quite complex. We report here some aspects of the reactions of the phosphines **4**, **5**, and PPh_3 with alkali metals in ether solvents. Additionally, the synthesis of 1 via Cl_2PNEt_2 and the reactions of 1 to yield **2** and $[P(p\text{-}C_6H_4NMe_2)_2]_2$ are described.

Results and Discussion

A summary of the reactions of the (p-(dimethylamino)phenyl)phosphine derivatives and the numbering system for the compounds are provided in Scheme I.

Synthesis of 1 and Its Reactions with Lithium. The only literature synthesis for 1 was reported over 50 years ago by the thermal decomposition of tris(p-(dimethylamino)phenyl)dichlorophosphorane (**3**).[12] In our laboratory we were unable to isolate 1 in this manner and, since details of the reaction are not available, this approach was not pursued further.

Although in principle the direct reaction of PCl_3 and LiC_6H_4-p-NMe_2 can lead to 1, we find that the trisubstituted product **5** is formed preferentially. This behavior is similar to that observed for the reaction of PhLi with PCl_3.[15] The approach to $ClP(p\text{-}C_6H_4NMe_2)_2$ given in eqs 1 and 2, however, proved successful.[16]

$$Cl_2PNEt_2 + 2Li\text{-}p\text{-}C_6H_4NMe_2 \xrightarrow[-78\ °C]{Et_2O} Et_2NP(p\text{-}C_6H_4NMe_2)_2 + 2LiCl \quad (1)$$

$$Et_2NP(p\text{-}C_6H_4NMe_2)_2 + 2HCl \xrightarrow[-100\ °C]{Et_2O} ClP(p\text{-}C_6H_4NMe_2)_2 + Et_2N{\cdot}HCl \quad (2)$$

The basis for this route is the observation that P–N bonds in phosphinous amides can be cleaved with dry HCl to yield chloro-substituted phosphines.[17] Bis(p-(dimethylamino)phenyl)phosphinous diethylamide, $Et_2NP(p\text{-}C_6H_4NMe_2)_2$, was synthesized by the dropwise addition of Cl_2PNEt_2 to an ether solution of Li-p-$C_6H_4NMe_2$ at −78 °C. The formation of $Et_2NP(p\text{-}C_6H_4NMe_2)_2$ was quantitative as determined by ^{31}P NMR spectra of the reaction mixture and the isolated product. Although the cleavage of P–N bonds with alkali metals in phosphinous amides has been reported in the literature,[18] we recovered $Et_2NP(p\text{-}C_6H_4NMe_2)_2$ unchanged after attempts to cleave with potassium or sodium.

The hydrochlorination reaction was effected by either anhydrous liquid HCl at −100 °C or dry HCl in ether solution from −80 to 0 °C. Analysis of the product suggested that it was isolated as the HCl salt (^{31}P NMR, 77 ppm).[19] This was confirmed by gravimetry and by the observation that the reaction with lithium required more than a stoichiometric amount of metal to yield $LiP(p\text{-}C_6H_4NMe_2)_2$. Protonation was determined to occur at the amine group since no phosphorus–proton coupling was observed in the ^{31}P NMR spectrum. Hydrolysis of 1 yielded a product that was characterized by a doublet in the ^1H-coupled ^{31}P NMR spectrum at 25.6 ppm (J_{PH} = 510 Hz). This product is assigned to bis(p-(dimethylamino)phenyl)phosphine oxide ($H(O)P(p\text{-}C_6H_4NMe_2)$) by analogy to $H(O)PPh_2$.[20]

$ClP(p\text{-}C_6H_4NMe_2)_2{\cdot}HCl$ reacted with lithium in refluxing THF to initially yield the diphosphine tetrakis(p-(dimethylamino)phenyl)diphosphine (**6**), which separated as a white powder from the reaction mixture. Compound **6** reacted further with lithium to give a 20–60% conversion to **2a**. Addition of potassium to the reaction mixture did not increase the conversion, which was low compared to the cleavage of tetraphenyldiphosphine.[11,21]

Reactions of 4 with Alkali Metals. As mentioned in the Introduction, the literature method for the preparation of $KP(p\text{-}C_6H_4NMe_2)_2$ (**2b**) involves the cleavage of **4** with potassium metal. When this reaction was monitored by ^{31}P NMR spectroscopy, we found that the cleavage proceeds at a much lower temperature and that the product composition is more complicated than previously indicated. In THF the reaction was quantitative after 2 h at room temperature. The ^{31}P NMR spectrum of the reaction mixture (prepared in 2-ethoxyethyl ether at 120 °C according to the literature conditions)[13] consisted of two singlets, at −12.3 and −20.6 ppm, in the approximate ratio of 8:1. When the reaction was performed in either THF or 2-ethoxyethyl ether at room temperature, the product ratio was 4:1. (In THF the observed shifts occur at −14.2 and −23.1 ppm.) A summary of the ^{31}P NMR results for a series of phosphine derivatives is given in Table I. It

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(19) Protonated derivatives containing p-$C_6H_4NMe_2$ give broadened signals by ^{31}P NMR spectroscopy that slowly move upfield. This is consistent with a shift to the left in the equilibrium (in $CDCl_3$)

$$-C_6H_4\text{-}p\text{-}NMe_2 + HCl \rightleftharpoons [-C_6H_4\text{-}p\text{-}NMe_2H]^+[Cl]^-$$

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Table I. ^{31}P NMR Chemical Shifts[a]

p-$C_6H_4NMe_2$ deriv		phenyl deriv	
compd	δ, ppm	compd	δ, ppm
$P(p\text{-}C_6H_4NMe_2)_3$ (**5**)	−11.2 (−10.8) {−11.5}[b]		
$P(Ph)(p\text{-}C_6H_4NMe_2)_2$ (**4**)	−9.1 (−8.6)	PPh_3	−6.5 {−5.4}[c]
$P(Ph)_2(p\text{-}C_6H_4NMe_2)$	−7.2 (−6.7)		
$KP(p\text{-}C_6H_4NMe_2)_2$ (**2b**)	−23.1 [−20.5]	$KPPh_2$	−10.0 {−12.4}[d]
$KP(Ph)(p\text{-}C_6H_4NMe_2)$	−14.2 [−12.3]		
$LiP(p\text{-}C_6H_4NMe_2)_2$ (**2a**)	−35.7	$LiPPh_2$	−21.8 {−23.0}[d]
$LiP(Ph)(p\text{-}C_6H_4NMe_2)$	−27.5		
$HP(p\text{-}C_6H_4NMe_2)_2$	−45.8, J_{PH} = 213 Hz	$HPPh_2$	−41.9, J_{PH} = 221 Hz {−40.7, J_{PH} = 216 Hz}[e]
$HP(Ph)(p\text{-}C_6H_4NMe_2)$	−43.6, J_{PH} = 212 Hz		
$Et_2NP(p\text{-}C_6H_4NMe_2)_2$	62.0	Et_2NPPh_2	{60.8}[e]
$ClP(p\text{-}C_6H_4NMe_2)_2\cdot HCl$	(77.0)	$ClPPh_2$	82.5 {81.5}[f]
$H(O)P(p\text{-}C_6H_4NMe_2)_2\cdot HCl$	25.6, J_{PH} = 510 Hz	$H(O)PPh_2$	22.1, 25.6 {J_{PH} = 513 Hz}[g]
$[P(p\text{-}C_6H_4NMe_2)_2]_2$ (**6**)	−20.4 (−19.2)	$(PPh_2)_2$	{−15.2}[h]
$C_6H_{11}P(p\text{-}C_6H_4NMe_2)_2$	−21.1 (−20.5)	$C_6H_{11}PPh_2$	−13.5

[a] Values without enclosures are from samples dissolved in THF, those in parentheses are in $CDCl_3$, and those in brackets are in 2-ethoxyethyl ether. Literature values in various solvents are given in braces. Shifts downfield from external 85% H_3PO_4 are positive. [b] Reference 36. [c] Reference 23. [d] Reference 22. [e] Reference 35. [f] Reference 37. [g] Reference 20. [h] Reference 38.

$$PhP(p\text{-}C_6H_4NMe_2)_2 + 2Li \xrightarrow[24\ h]{THF,\ 20\ °C} LiP(p\text{-}C_6H_4NMe_2)_2\ (67\%) + LiPh + LiP(Ph)(p\text{-}C_6H_4NMe_2)\ (18\%) + Li\text{-}p\text{-}C_6H_4NMe_2 + LiPPh_2\ (4\%) + Li(p\text{-}C_6H_4NMe_2) + PPh_2(p\text{-}C_6H_4NMe_2)\ (6\%) \quad (4)$$

can be seen from the values in this table that the presence of the electron-donating p-NMe_2 groups results in an upfield shift compared to the signals for the phenyl analogues. Thus, of the two products observed, the minor product with a chemical shift of −23.1 ppm is most consistent with $KP(p\text{-}C_6H_4NMe_2)_2$. The chemical shift reported for the phenyl analogue $KPPh_2$ is −12.4 ppm.[22] When an aliquot of the phosphide solution was hydrolyzed with water, two doublets at −43.6 and −45.8 ppm, in a ratio identical with that of the original cleavage products, were observed in the ^1H-coupled ^{31}P NMR spectrum. These chemical shifts and the coupling constants (213.5 and 212.6 Hz, respectively) are within the expected range for secondary phosphines.[23]

The main phosphide product from the cleavage reaction is identified as $KP(Ph)(p\text{-}C_6H_4NMe_2)$. The signal of lower intensity corresponds well to $KP(p\text{-}C_6H_4NMe_2)_2$ (eq 1). These assignments are confirmed by the results obtained for both the cleavage of **5** (vide infra) and the hydrolysis of $LiP(p\text{-}C_6H_4NMe_2)_2$ (**2a**). The products obtained upon hydrolysis of the mixture in reaction 3 are thus $HP(p\text{-}C_6H_4NMe_2)_2$ and $HP(Ph)(p\text{-}C_6H_4NMe_2)$.

$$PhP(p\text{-}C_6H_4NMe_2)_2 + K \xrightarrow[2\ h]{THF,\ 20\ °C} \underset{80\%}{KP(Ph)(p\text{-}C_6H_4NMe_2)} + \underset{20\%}{KP(p\text{-}C_6H_4NMe_2)_2} \quad (3)$$

The unexpected product composition in the reaction of **4** with potassium led us to investigate the behavior of other alkali metals in the cleavage reaction. In agreement with the literature, sodium was found to be ineffective in the cleavage of **4** in refluxing THF.[13] However, we found that lithium reacts readily. The ^{31}P NMR spectrum of the reaction mixture that results after 1 day of stirring **4** and Li metal at room temperature showed 90% conversion to phosphides. Interestingly, the product composition was very different from that observed with potassium. The major product has a ^{31}P NMR signal at −35.6 ppm, which represents 67% of the total integrated intensity. Three minor products were seen to give singlets at −27.5, −21.8, and −7.2 ppm with relative intensities of 18, 4, and 6%, respectively. When an aliquot of the phosphide solution was quenched with water, the corresponding secondary phosphines were formed. These were $HP(p\text{-}C_6H_4NMe_2)_2$ (67%) and $HP(Ph)(p\text{-}C_6H_4NMe_2)$ (18%). The intensities observed for these secondary phosphines are in good agreement with the two major peaks of the starting phosphide reaction mixture. The third secondary phosphine signal expected from the hydrolysis of the phosphide in smallest quantity was not observed due to a poor signal-to-noise ratio. However, by independent synthesis the third phosphide signal observed in the ^{31}P NMR spectrum is assigned to $LiPPh_2$. The chemical shift of the fourth component of the original mixture is not in the range expected for a phosphide and is assigned to $PPh_2(p\text{-}C_6H_4NMe_2)$. The ^{31}P chemical shift of $PPh_2(p\text{-}C_6H_4NMe_2)$ was independently confirmed by the synthesis of this species. The cleavage of $P(Ph)(p\text{-}C_6H_4NMe_2)_2$ with lithium in THF is summarized in eq 4.

By comparison with the products from the reaction of **1** with lithium the main phosphide peak at −35.6 ppm and the secondary phosphine signal derived from it upon hydrolysis at −45.8 ppm were identified as $LiP(p\text{-}C_6H_4NMe_2)_2$ and $HP(p\text{-}C_6H_4NMe_2)_2$, respectively.

The formation of $LiPPh_2$, indicated by the signal at −21.8 ppm, and $Ph_2P(p\text{-}C_6H_4NMe_2)$, indicated by the signal at −7.2 ppm, was unexpected and suggests a complex equilibrium that may be represented as eq 5.

$$LiP(Ph)(p\text{-}C_6H_4NMe_2) + LiPh \rightleftarrows Ph_2P(p\text{-}C_6H_4NMe_2) + 2\ Li \rightleftarrows LiP(p\text{-}C_6H_4NMe_2) + LiPPh_2 \quad (5)$$

Reaction of 5 with Potassium. After the observation of the preferred cleavage of a p-(dimethylamino)phenyl–P bond in **4** with potassium, reconsideration of **5** as a starting

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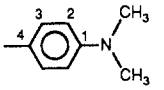
Table II. ^{13}C NMR Data

compd	chem shift,[a] ppm (N)CH_3	C_1	C_2	C_3	C_4
$KP(p\text{-}C_6H_4NMe_2)_2$[b]	42.26 (s)	145.81 (s)	115.35 (d) J_{PCCC} = 5.1 Hz	131.09 (d) J_{PCC} = 17.7 Hz	145.69 (d) J_{PC} = 46.19 Hz
$KPPh_2$[b]		129.01	127.79 (d) J_{PCCC} < 3 Hz	129.47 (d) J_{PCC} = 18.9 Hz	157.59 (d) J_{PC} = 51.5 Hz
$HP(p\text{-}C_6H_4NMe_2)_2$[b]	40.35 (s)	151.63 (s)	113.30 (d) J_{PCCC} = 2.6 Hz	135.78 (d) J_{PCC} = 18.0 Hz	121.74 (d) J_{PC} = 5.8 Hz
$C_6H_{11}P(p\text{-}C_6H_4NMe_2)_2$[c]	40.2 (s)	150.42 (s)	112.33 (d) J_{PCCC} = 7.3 Hz	133.59 (d) J_{PCC} = 19.0 Hz	125.06 (d) J_{PC} = 7.6 Hz
Li-p-$C_6H_4NMe_2$	41.20 (s)[d] 41.71 (s)[b]	150.66 (s) 149.2 (s)	113.48 (s) 112.70 (s)	142.65 (s) 144.76 (s)	157.89 (s) 159.2 (s)
LiPh[d]		127.2 (s)	128.0 (s)	143.1 (s)	174.1 (s)
$C_6H_5NMe_2$[b]	40.62 (s)	151.73 (s)	113.28 (s)	129.5 (s)	117.09

[a] Carbon atoms numbered in the following manner:  [b] Solvent THF. [c] Solvent $CDCl_3$. [d] Solvent Et_2O.

material for the synthesis of **2b** is obvious. Thus, we find that potassium reacts with **5** to yield $KP(p\text{-}C_6H_4NMe_2)_2$ at room temperature in THF (eq 6). The formation of

$$P(p\text{-}C_6H_4NMe_2)_3 + K \xrightarrow[24\ h]{THF,\ 20\ °C} KP(p\text{-}C_6H_4NMe_2)_2 \quad (6)$$

$KP(p\text{-}C_6H_4NMe_2)_2$ (^{31}P NMR, −23.1 ppm) was quantitative, as determined by ^{31}P NMR spectroscopy, after 1 day under the conditions shown.

In spite of the fact that potassium prefers the cleavage of a p-(dimethylamino)phenyl–P bond in **4**, the reaction of potassium with **5** is approximately 12 times slower than with **4** and about 60 times slower than with PPh_3. (A quantitative reaction of PPh_3 with potassium takes place in about 20 min in THF (vide infra).) Sodium and lithium were ineffective in the cleavage of **5**, as could be expected from the literature[13] and the results presented above for **4**.

The reactions represented by eqs 3 and 6 above are shown without the formation of $K(p\text{-}C_6H_4NMe_2)$, which may be expected as a byproduct from the cleavage with potassium. NMR and mass spectral analysis of solutions after hydrolysis, however, suggests that $K(p\text{-}C_6H_4NMe_2)$ is not present in these reaction mixtures. Also the chemical reactivity of the mixtures is most consistent with the absence of this anion. For example, when reaction 6 was performed in THF as above, the ^{13}C NMR spectrum of the reaction mixture showed the presence of dimethylaniline but signals for $K(p\text{-}C_6H_4NMe_2)$ were not detected. (It should be noted that $Li(p\text{-}C_6H_4NMe_2)$ could be detected in the mixtures obtained from reaction 4 above.) The ^{13}C NMR results for the series of compounds reported here are summarized in Table II.

Hydrolysis of an aliquot of the reaction mixture with D_2O yielded only $DP(p\text{-}C_6H_4NMe_2)_2$. Conversely, when the reaction was performed in THF-d_8 and hydrolysis was accomplished with H_2O, then $HP(p\text{-}C_6H_4NMe_2)_2$ and $D(p\text{-}C_6H_4NMe_2)$ were obtained. (The secondary phosphine $HP(p\text{-}C_6H_4NMe_2)_2$ can be converted slowly back to $KP(p\text{-}C_6H_4NMe_2)_2$ upon addition of more potassium.) When the reaction mixture from eq 6 was used directly with alkyl halides such as hexyl and ethyl bromide, only the desired alkylphosphines were obtained. The only aniline-containing derivative formed that was not a phosphine was dimethylaniline itself. Before it was realized that $K(p\text{-}C_6H_4NMe_2)$ was absent from the reaction mixture, *tert*-butyl chloride (1 equiv) was added in several instances to the mixture from eq 6. The purpose, of course, was to destroy the $K(p\text{-}C_6H_4NMe_2)$ that was thought to be present; the result, however, was the immediate formation of $HP(p\text{-}C_6H_4NMe_2)_2$ and $(CH_3)_2C{=}CH_2$.

The presence of dimethylaniline, which also was observed as a byproduct from the potassium cleavage of **4** in 2-ethoxyethyl ether, suggests that the nucleophilic ring opening of THF by $K(p\text{-}C_6H_4NMe_2)$ can be excluded. The expected product of such a ring-opening reaction, p-(4-hydroxybutyl)(dimethylamino)benzene, was not present in any of the reaction solutions. To obtain dimethylaniline in these reactions, THF must serve as the hydrogen source. If the reaction is radical in nature, then a hydrogen atom is abstracted, and if $K(p\text{-}C_6H_4NMe_2)$ is the reaction intermediate, then THF serves as a proton source. Unfortunately the decomposition products of THF could not be unambiguously identified.

Reaction of Triphenylphosphine with Potassium in Ether Solvents. The formation of diphenylphosphide can be achieved via the cleavage of a P–C bond in triphenylphosphine with alkali metals under a variety of conditions.[10,24–27] This is accomplished most suitably with lithium in ether solvents or sodium in liquid ammonia, although potassium in dioxane is also effective in the cleavage of some tertiary phosphines.[14b,22,25]

$$PPh_3 + 2M \rightarrow MPPh_2 + MPh \quad (7)$$

$$M = Li, Na, K$$

In addition to PPh_2^-, the cleavage reaction is reported to generate the phenyl anion as indicated in eq 7.[10] Before the phosphide may be used in a nucleophilic substitution reaction, the phenyl anion must be selectively destroyed.[26] When the reaction is performed in liquid ammonia, an acid such as NH_4Br is used, while in ether solvents *tert*-butyl chloride is the reagent of choice. *tert*-Butyl chloride is unable to undergo substitution; thus, it reacts with phenyl anions to yield benzene and 2-methylpropene.

When the cleavage of PPh_3 with potassium metal in THF was monitored by ^{31}P NMR spectroscopy, the reaction was determined to be complete in approximately 20

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min at room temperature. The ^{13}C NMR spectrum of the reaction mixture showed no direct evidence for the presence of KPh. After hydrolysis of the reaction mixture $HPPh_2$ was obtained as the principle phosphorus-containing product. Analysis of the organic products after reaction with excess ethyl bromide by GC–MS methods revealed a complex mixture that includes benzene, hydroxybutenes, biphenyl, ethoxybenzene, and traces of ethylbenzene. When KPh was prepared directly by a literature method[28] and dissolved in THF, a similar product distribution was obtained. The product mixture is consistent with some radical character for KPh. Thus, in principle, potassium diphenylphosphide generated from potassium metal and triphenylphosphine may be used directly in the subsequent synthesis of phosphines without the intentional destruction of the phenyl anion. However, this method is not desirable for the synthesis of phosphines, since the reaction with alkyl halides leads to relatively large quantities of the diphosphine $(PPh_2)_2$.

Also, in contrast to the case for $KP(p\text{-}C_6H_4NMe_2)_2$ the reactivity of $KPPh_2$ toward *tert*-butyl chloride is slow. At room temperature the reaction between $KPPh_2$ and $C(CH_3)_3Cl$ required 3 h to come to completion (the products were $HPPh_2$ and $(CH_3)_2CCH_2$), whereas the reaction of $C(CH_3)_3Cl$ with $KP(p\text{-}C_6H_4NMe_2)_2$ was complete in a few minutes.

Cleavage Site of Tertiary Phosphines and the Fate of Potassium Aryls. Although the formation of potassium aryls is assumed in the cleavage reactions of triarylphosphines,[10] it is apparent from the work presented here that these anions have only a transient existence in ether solvents. This is to be expected from the reported reactivity of phenylpotassium and phenylsodium.[28,29] The phenyl anions may be isolated as extremely air-sensitive solids that dissolve with concomitant reaction in ether solvents. As noted above, the reaction of solid phenylpotassium with THF yields the same product distribution of phenyl-containing products as observed in the cleavage of triphenylphosphine. Thus, any KC_6H_5 or $K(p\text{-}C_6H_4NMe_2)$ formed in the cleavage reactions of **4** or **5** reacts immediately with THF to yield predominantly benzene or dimethylaniline, respectively. The reactions of phenylpotassium, in particular, appear to have some radical character as evidenced by the range of observed products. This is consistent with the ESR spectrum of the cleavage products of pentaphenylphosphole with potassium in THF or dimethoxyethane.[30]

The cleavage of tertiary phosphines generally occurs at the most electron-withdrawing substituent.[14] In the case of the cleavage of $PhP(p\text{-}C_6H_4NMe_2)_2$ this expectation is met when lithium is used as the alkali metal. However, potassium preferentially cleaves the most electron-donating substituent. Potassium is exceptional in this regard for other cleavage reactions also. Thus, the cleavage of PEt_2Ph and $P(c\text{-}C_6H_{11})_2Ph$ with potassium yields KPEtPh and $KP(c\text{-}C_6H_{11})Ph$, respectively,[14b] while $PEtPh_2$ is cleaved with potassium to give the expected product, KPEtPh.[14b]

If one takes the relative rates of the formation of the anions as an estimate of their relative stability, then the order PPh_2^- > $[P(Ph)(p\text{-}C_6H_4NMe_2)]^-$ > $[P(p\text{-}C_6H_4NMe_2)_2]^-$ is obtained. The last of these, which is formed most slowly, is the most reactive as expected. The strong electron-donating groups NMe_2 make the $[P(p\text{-}C_6H_4NMe_2)_2]^-$ anion a strong nucleophile. (The relative stability of the corresponding potassium aryls is not important here, since these react immediately with solvent.) This order of reactivity is also maintained when the alkali-metal cation is lithium. Also, as expected, $KP(p\text{-}C_6H_4NMe_2)_2$ is more reactive as a nucleophile toward alkyl halides than its lithium analogue $LiP(p\text{-}C_6H_4NMe_2)_2$. This is consistent with the expectation that lithium phosphides should have more covalent character than potassium phosphides. The phosphide $KPPh_2$ appears to have some radical character, as judged by its reactivity with alkyl halides; as noted above, substantial amounts of the diphosphine P_2Ph_4 are obtained in these reactions.

The cleavage of $PhP(p\text{-}C_6H_4NMe_2)_2$ with lithium metal yields an equilibrium mixture of phosphides, including PPh_2^-, which must arise from an aryl scrambling reaction. The scrambling may occur in the lithium reactions, since the lithium aryls are stable in ether solvents whereas the potassium aryls are not. The product distribution is determined not only by the relative stability of the phosphides, as above, but also by the relative stability of the lithium aryls that are also formed. Because of the electron-donating character of the dimethylamine group, LiPh is expected to be more stable than $Li(p\text{-}C_6H_4NMe_2)$.

The success in the cleavage of the diphosphines P_2Ph_4 and $(p\text{-}C_6H_4NMe_2)_2PP(p\text{-}C_6H_4NMe_2)_2$ follows the expected trend in that electron-donating substituents on the phenyl rings decrease the efficiency of the reaction.[31] Nevertheless, because of the poor solubility of $(p\text{-}C_6H_4NMe_2)_2PP(p\text{-}C_6H_4NMe_2)_2$ in ether solvents, this method yields pure $LiP(p\text{-}C_6H_4NMe_2)_2$ and serves as an independent route to verify the results obtained in the cleavage of **5**.

Conclusion

From the investigation of the cleavage of **4**–**6** with different alkali metals to yield phosphides, it is concluded that it is difficult to predict the success of a particular phosphine cleavage reaction. The product distribution depends not only on the stability of the aryl and phosphide anions generated but also on the choice of alkali metal used for the reaction.

Among the possible synthetic paths to $[P(p\text{-}C_6H_4NMe_2)_2]^-$ the cleavage of **5** with potassium provides the shortest and cleanest method. The increased nucleophilic character of $KP(p\text{-}C_6H_4NMe_2)_2$ compared to that of $KPPh_2$ and $LiPPh(p\text{-}C_6H_4NMe_2)$ and the absence of potassium aryls in the reaction mixture lead to a convenient synthesis of a variety of phosphines that contain amine functional groups. This is an important synthetic application of the previously less considered organopotassium reagents.

Experimental Section

Microanalyses were performed by Galbraith Laboratories, Knoxville, TN. Proton, ^{13}C, and ^{31}P NMR spectra were run at 25 °C on a Bruker WP-200 instrument. ^{31}P NMR chemical shifts are referenced to external 85% H_3PO_4. Direct-probe and GC mass spectra were recorded on a VG Analytical 7070 E-HF spectrometer at 70 eV. A Supelco SP2100 packed column (6 ft, 2 mm i.d., temperature programmed from 60 to 200 °C) was used to separate the organic products from the hydrolysis reactions. All preparations and operations were carried out under a deoxygenated

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dry argon atmosphere. Solvents were dried and degassed by standard techniques before use.

Phosphorus trichloride, PPh_3, *p*-bromo-*N,N*-dimethylaniline, lithium (1% sodium), potassium, *n*-hexyl bromide, ethyl bromide, and chlorobenzene were purchased from Aldrich and used as received. Dichlorophenylphosphine, hexaethylphosphorous triamide, and *tert*-butyl chloride (Aldrich) were freshly distilled before use.

Compounds **4** and **5** were prepared directly from Li(*p*-$C_6H_4NMe_2$)[32] and either Cl_2PPh or PCl_3 by literature methods.[33] Cl_2PNEt_2 was prepared from PCl_3 and $P(NEt_2)_3$ by the literature method[34] and freshly distilled before use.

Preparation of Potassium Bis(*p*-(dimethylamino)-phenyl)phosphide (2b). To a stirred suspension of 10.0 g (25.5 mmol) of tris(*p*-(dimethylamino)phenyl)phosphine (**5**) in 200 mL of THF was added 2.10 g (53.7 mmol) of finely cut potassium chips. The phosphide formation started immediately, resulting in a dark red color and a slow, but complete, dissolution of **5**. The mixture was stirred for 1 day at room temperature. Aliquots taken from the solution showed quantitative transformation as determined by ^{31}P NMR spectroscopy (s, −23.1 ppm). The phosphide solution was used for the reactions with alkyl halides or with water after the removal of the unreacted potassium. Cleavage of phenylbis(*p*-(dimethylamino)phenyl)phosphine (**4**) and PPh_3 was performed in a similar manner with potassium or lithium.

Preparation of Bis(*p*-(dimethylamino)phenyl)phosphinous Diethylamide. Dichlorophosphinous diethylamide, Cl_2PNEt_2 (10.9 g, 0.0625 mol), was added dropwise with vigorous stirring at −78 °C to an ether solution of *p*-lithio-*N,N*-dimethylaniline prepared from 25.0 g of *p*-bromo-*N,N*-dimethylaniline (0.0125 mol) and 1.82 g of lithium (0.262 mol) by the literature method.[32] Stirring was continued after the addition was complete, and the suspension was allowed to reach room temperature. The separated salts were removed by filtration, and the solution was concentrated under vacuum to 25% of its original volume. After a second filtration the solvent was removed completely to yield 21.0 g of an extremely moisture-sensitive white crystalline product: yield 97%; mp 35–40 °C; ^1H NMR (200.1 MHz, $CDCl_3$, ppm) 0.95 (t, J_{HH} = 7 Hz, NCH_2CH_3), 2.96 (s, NCH_3), 3.05 (d qt, J_{HH} = 7 Hz, J_{PNCH} = 9.7 Hz, NCH_2CH_3), 6.70 (d d, J_{HH} = 8.8 Hz, J_{PCCCH} = 1.1 Hz), 7.28 (d d, J_{HH} = 8.8 Hz, J_{PCCH} = 6.8 Hz).

Acidic Cleavage of $Et_2NP(p\text{-}C_6H_4NMe_2)_2$. Anhydrous liquid HCl (4.55 g, 0.125 mol) was condensed in a small flask on a vacuum line and added to an ether solution containing 21.0 g of $Et_2NP(p\text{-}C_6H_4NMe_2)_2$, prepared as above, at −100 °C. The reaction mixture was then allowed to reach room temperature with continuous stirring. the precipitated salts were removed and washed with 3 × 100 mL of ether. Removal of the ether solvent yielded from 7.15 to 11.3 g (37–59%) of the moisture-sensitive yellow crystalline product $ClP(p\text{-}C_6H_4NMe_2)_2 \cdot n$HCl ($n$ = 0–2). Anal. Calcd for n = 1: Cl, 20.6. Found: Cl, 20.58. Mp: 60–80 °C. ^1H NMR (200.1 MHz, $CDCl_3$, ppm): 2.92–3.06 (br s), 6.9 (unresolved multiplet), 7.44 (d d, J_{HH} = 8.4 Hz, J_{PCCH} = 8.4 Hz). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, ppm): 40.01 (br s), 111.92 (br s), 117.0 (s, phosphorus coupling not resolved), 134.59 (d, J_{PCC} = 23.0 Hz, 151.92 (br s).

Reaction of 1·HCl with Lithium. In a typical experiment 6.90 g (22.5 mmol) of $ClP(p\text{-}C_6H_4NMe_2)_2$·HCl was dissolved in 100 mL of THF and 0.39 g of finely cut lithium (56 mmol) was added. The mixture was then brought to reflux for 4–8 h. After a short period of time a white precipitate of **6** formed. Continued reflux converted some of **6** to **2a**. When the reaction was monitored by ^{31}P NMR spectroscopy, conversions of 20–60% to the phosphide **2a** could be observed. The diphosphine **6** could be isolated by filtration, while the solutions of **2a** could be used directly in subsequent synthetic reactions. $(p\text{-}C_6H_4NMe_2)_2PP(p\text{-}C_6H_4NMe_2)_2$: mp 213–216 °C; ^1H NMR (200.1 MHz, $CDCl_3$, ppm) 2.88 (s), 6.56 (d, J_{HH} = 8.6 Hz), 7.27 (d d, d d, J_{HH} = 8.6 Hz, J_{PCCH} = 2.6 Hz, J_{PPCCH} = 2.6 Hz); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, ppm) 40.30 (s), 112.21 (s), 122.25 (s), 135.30 (d d, J_{PCC} = J_{PPCC} = 13.6 Hz), 150.43 (s); mass spectrum (70 eV, m/e) M^+ 542 (10%), $[P(p\text{-}C_6H_4NMe_2)_3]^+$ 391 (3%), $[P(p\text{-}C_6H_4NMe_2)_2]^+$ 271 (80%), $[P(p\text{-}C_6H_4NMe_2)]^+$ 151 (100%). Anal. Calcd for $C_{32}H_{40}N_4P_2$: C, 70.84; H, 7.38; N, 10.33; P, 11.44. Found: C, 70.38; H, 7.35; N, 10.28; P, 11.02.

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