J. Org. Chem. **2000,** *65,* 951−957

Mechanism of Phosphorus−Carbon Bond Cleavage by Lithium in Tertiary Phosphines. An Optimized Synthesis of 1,2-Bis(phenylphosphino)ethane

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Received May 3, 1999

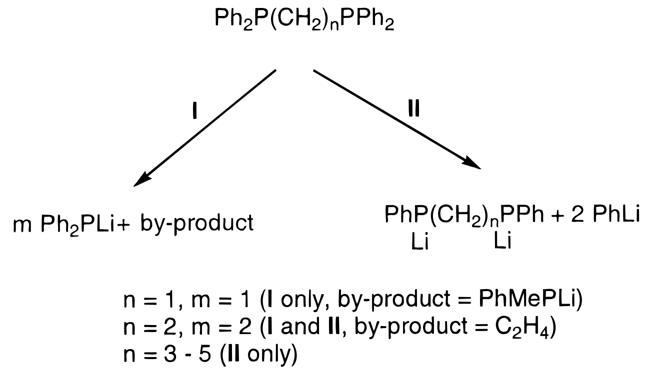
Conditions influencing the extent of P−C$_{aryl}$ vs P−C$_{alkyl}$ bond cleavage in the reaction of $Ph_2P(CH_2)_2PPh_2$ with lithium in THF have been investigated. The results complement and elucidate earlier work; they indicate that the mechanism of P−C bond cleavage in tertiary phosphines of this type involves a thermodynamic equilibrium between P−C$_{aryl}$ and P−C$_{alkyl}$ cleaved radicals and anions, followed by reaction and stabilization of these as lithium salts. The addition of water to the reaction mixture causes a reestablishment of the cleavage equilibrium prior to the formation of the secondary phosphines. A mechanism involving competitive release of leaving groups as the thermodynamically most stable anion or radical has been proposed. The preparation of (R*, R*)-(±)/(R*, S*)-PhP(H)-$(CH_2)_2$P(H)Ph by this route has been optimized.

Introduction

Despite its synthetic importance, the mechanism of the phosphorus−carbon bond cleavage that occurs when a tertiary phosphine reacts with an alkali metal in tetrahydrofuran is poorly understood, with many of the experimental procedures employed in these reactions being optimized by trial and error. An important example concerns the preparation of 1,2-bis(phenylphosphino)ethane, **1**, from 1,2-bis(diphenylphosphino)ethane, **2**. Early syntheses of **1** are cumbersome and low yielding,[1−4] so that the alkali metal cleavage of phosphorus-phenyl groups[5] from commercially available **2**, followed by protonation of the resulting bis(phosphide), is the most convenient synthesis.[6] In the reaction, P−C cleavage is effected most successfully by lithium to produce PhP(Li)-CH_2CH_2P(Li)Ph, **4**, although substantial quantities of $LiPPh_2$, **3**, are generated by competitive cleavage of P−C$_{alkyl}$ bonds.

A systematic investigation of lithium-induced P−C bond cleavage in $Ph_2P(CH_2)_nPPh_2$ (n = 1−5) has been carried out, where it was observed that the regioselectivity of the reaction at room temperature in THF depended on the value of n (Scheme 1).[7] For n = 1, P−C$_{alkyl}$ cleavage (pathway I) occurred, but for n = 3−5, P−C$_{aryl}$ cleavage (pathway II) predominated. In the reaction of lithium with **2** (n = 2) a mixture of products from pathways I and II was obtained; the presumed intermediate for pathway I, $[Ph_2PCH_2CH_2^-Li^+]$, was not observed, nor was Ph_2PEt, which would have been formed by protonation of the anion by the solvent. It was therefore assumed that the intermediate decomposed to give Ph_2PLi and ethylene, the latter being detected.[7]

Scheme 1



The cleavage reactions are erratic with respect to induction times and amounts of unreacted starting material. The diphosphides $PhP(Li)(CH_2)_nP(Li)Ph$ (n = 2−5) are also highly reactive. For example, the addition of *tert*-butyl chloride to the reaction mixtures to remove the PhLi byproduct resulted in the formation of the corresponding 1,2-bis(*tert*-butyl)-substituted diphosphines.[7] This contrasts with the behavior of Ph_2PLi, which does not react with *tert*-butyl chloride.[5] Alkylation of the bis(phosphides) clearly competes with deprotonation of the *tert*-butyl chloride by the phenyllithium. At reduced temperatures, however, alkylation at phosphorus is minimized.[6,7]

These data were rationalized in terms of the relative electronic stabilization of the phosphide ions by the substituents. Because of its ability to delocalize negative charge, a phenyl group stabilizes an anion better than a methyl group, similar to an ethyl group but more poorly than an n-propyl, n-butyl, or n-pentyl group.[7] As an aryl group is necessary before tertiary phosphines react with

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10.1021/jo9907336 CCC: \$19.00

lithium,[7] it was suggested that the key process in these heterogeneous cleavage reactions involves an aryl-mediated association of the phosphine with the metal surface, followed by a slow step (or steps) leading to bond cleavage (eq 1).

$$Ph_2RP \xrightarrow{Li} Ph_2RP^{-\bullet}\,Li^+ \longrightarrow PhRP^-\,Li^+ + Ph^\bullet \xrightarrow{Li} PhRP^-\,Li^+ + Ph^-\,Li^+ \qquad (1)$$

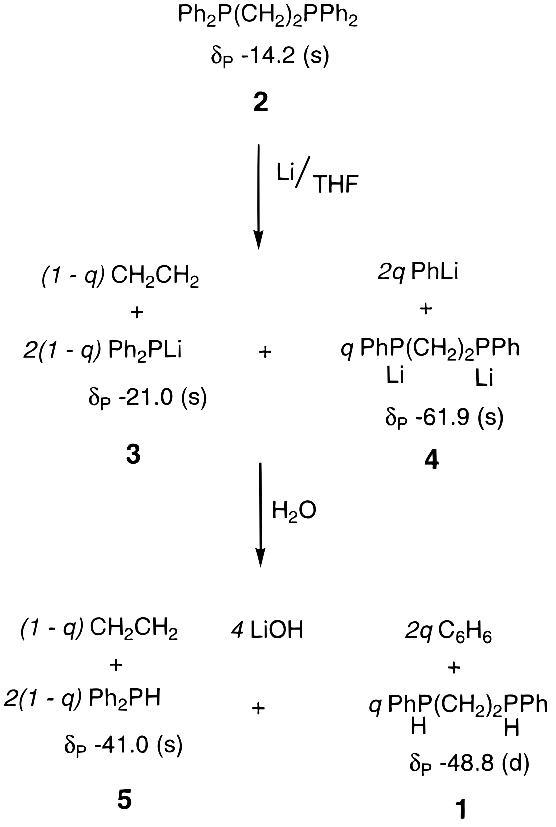
Although this mechanism accounts for P$-$C$_{alkyl}$ cleavage in bis(tertiary phosphines) having $n = 1$, it does not explain P$-$C$_{aryl}$ cleavage for $n = 3-5$ because of the less stable radical produced. The alternative explanation involving release of an organic group as an anion is, however, also inconsistent with the leaving group preferences.

ESR studies of related reactions have indicated that some of the $R_2P^-Li^+$ (R = Me, *n*-Pr, *n*-Bu, Ph) produced in similar cleavage reactions react with excess lithium to give $R_2P^{2-\bullet}(Li^+)_2$, which were detected as the only spin-active species in solution.[8,9] These short-lived radical dianions apparently propagate by rapid intermolecular exchange at room temperature since bimolecular or other termination products have not been observed.[9] Low levels of radical dianions may also be responsible for the characteristic red color of the bis(arylphosphine)-lithium reaction mixtures described above.[7]

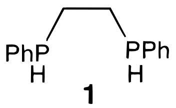
From these observations, it became evident that a means of synthesizing **1** in high yield lay in adjusting the conditions of the reactions in Scheme 2 so as to maximize the formation of the bis(phosphide) **4** (pathway II) and to minimize that of the competing mono(phosphide) **3** (pathway I). It has been reported[10] that crystalline **4** is hydrolyzed by water to give **1** in 68% overall yield.[11] Isolation of the solid on a large scale is troublesome, however, so that a high yielding in situ preparation of **1** from **2** would be desirable. Thus, a recent method of preparing **1** involved stirring a mixture of **2** and lithium wire in THF at 0 °C for 7 d and then treating the resulting mixture with water, which gave **1** in >80% yield.[12] The conditions for the lithiation were a carefully chosen compromise: the initial mixture was stirred for long enough to overcome the erratic induction time for P$-$C$_{aryl}$ cleavage, while the reduced temperature suppressed the formation of Ph_2PLi, **3**.

In our recent work concerning the optical resolution of the linear tetra(tertiary phosphine) (R^*,R^*)-(±)-1,1,4,7,-10,10-hexaphenyl-1,4,7,10-tetraphosphadecane,[13] we required considerable quantities of **1** as a starting material. Although high yields of **1** could be obtained by the literature method,[12] the process was capricious and reaction times of >7 d were sometimes required. A lower yielding but less time-consuming and more reliable route was subsequently developed and reported,[13] wherein a concentrated mixture of **2** and lithium in THF was heated under reflux for 3 h, the solution was filtered, and the filtrate cooled to room temperature. The crystalline **4**·4THF that deposited overnight was then quenched with ammonium bromide to give **1** in 65% yield.

Scheme 2



Despite the success of this procedure, it was clear that the trial-and-error approach hitherto adopted for the optimization of the reaction conditions required for the synthesis of **1** was unsatisfactory. Here we present a detailed investigation employing $^{31}P\{^1H\}$ NMR, UV$-$visible, and ESR spectroscopy to probe the factors influencing the conversion of **2** into **1**.



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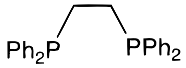

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Results and Discussion

Methodology. A series of reactions of the type shown in Scheme 2 were performed under different conditions of temperature and concentration, and their progress was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. This permitted the identification of the phosphines and phosphides present in the reaction mixtures, because, as previously noted, the presence of small quantities of radical dianions does not affect the $^{31}P\{^1H\}$ NMR chemical shifts.[7] Each NMR sample was collected and sealed (under inert atmosphere) in an NMR tube containing 1 drop of benzene-d_6, which was required to lock the NMR signal. To correlate the resonances obtained with the species shown in Scheme 2, each compound and intermediate was prepared and its $^{31}P\{^1H\}$ NMR chemical shift was determined in THF/benzene-d_6. The NMR data are given in Scheme 2 and agree with literature values.[7] The

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unsymmetrical compounds $Ph_2P(CH_2)_2P(Li)Ph$ and $Ph_2P(CH_2)_2P(H)Ph$ were not prepared, but resonances for them (δ −14.6, −41.9, and −15.45, −49.8, respectively[7]) were not evident in any of the experiments. A delay of 50 s between pulses was applied in recording the $^{31}P\{^1H\}$ NMR spectra in order to obtain accurate integrations.

Experiments. Initial experiments involved the reaction of **2** with lithium as described in ref 13. The addition of a 10-fold excess of finely divided lithium wire to a vigorously stirred solution of **2** in THF (0.20 mol L^{-1}) at 20 °C, followed by stirring of the mixture for 2 h, led to pale red solutions that contained significant quantities of the bis(phosphide) **4** (ca. 10−50%) and mono(phosphide) **3** (ca. 10−40%), in addition to **2** (ca. 10−80%). Solutions prepared in this way became slightly warm when the lithium was added; bubbles of ethene were not evident when **3** was the major product. The amounts of **3** and **4** in the mixtures increased over 3 d, but in an erratic manner. Thus, after 3 d, yields of **3** and **4** were 20−90%. For reactions that were essentially complete within 2 h of the addition of lithium, the proportions of **3** and **4** did not change with continued stirring for 3 d. Moreover, heating of these mixtures to 40 °C or cooling them to 0 °C for several hours did not result in significant changes in the relative proportions of **3** and **4**.

Concentration Dependence. Experiments at concentrations of **2** within the range 0.02−0.20 M and with 4.3- to 10-fold excesses of lithium produced similar quantities of **3** or **4**, within experimental error. For solutions below 0.02 M in **2**, accurate NMR determinations of species concentrations could not be achieved.

Temperature Dependence. When the reaction was carried out at 40 °C (0.20−0.02 M **2**, 10-fold Li), larger proportions of **3** were obtained (>30%).[6] At 0 °C, solutions enriched in the bis(phosphide) **4** were obtained.[6] Because temperature was clearly a critical factor, a solution of **2** in THF was added dropwise to a cooled (0 °C) and vigorously stirred suspension of lithium in THF.[6,14] After 1 h, stirring was stopped, and the mixture was allowed to warm to room temperature. The resulting solution contained **4** and **2** only. The reaction mixture was then heated under reflux for 2 h, after which the sample displayed the NMR resonance of **4** only. The results were reproducible within the concentration range examined, provided that the addition of **2** was carried out slowly and in sufficient local dilution. When the reaction was complete, unreacted lithium was removed by filtration of the hot mixture. Yellow crystals of $PhP(Li)CH_2CH_2P(Li)Ph{\cdot}4THF$, **4**·4THF, separated from the cold filtrate.[10,11]

UV−visible Spectroscopy. The UV−visible spectrum of the reaction mixture at completion contained absorptions at 366 nm (yellow) and 421 nm (red). The 366 nm band was due to $PhP(Li)CH_2CH_2P(Li)Ph$, **4**, which was verified by recording the spectrum of **4**·4THF under similar conditions. Because the major byproduct of the reaction, PhLi, is colorless,[15] the 421 nm absorption is most likely due to a radical dianion, as previously assumed.[7] The known radical dianion $Ph_2P^{2-\bullet}(Li^+)_2$, **6**, absorbs intensely at 429 nm in THF.[9] Furthermore, when a degassed solution of THF containing a trace of water was added dropwise to the solution of **4** at 0 °C, the peak at 421 nm was selectively diminished in intensity, consistent with the higher reactivity of the radical dianion.

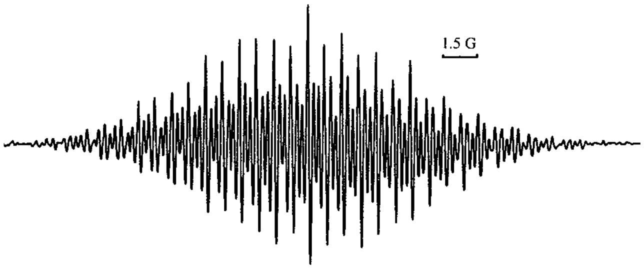

Figure 1. ESR spectrum at 20 °C of a solution of **4** prepared by the addition of a dilute THF solution of **2** to a suspension of lithium in THF at 0 °C ($g = 2.051$).

ESR Spectroscopy. The ESR spectrum of a solution of freshly prepared **4** exhibited a symmetrical pattern of peaks, suggesting the presence of a single spin-active species (Figure 1). The spectrum consists of at least 33 triplets, each separated by 0.75 G, and displays a monomodal, Gaussian-like distribution of intensities. The hyperfine splitting for each triplet is 0.25 G.

Previous investigations of $R_2P^{2-\bullet}(Li^+)_2$ indicated ^{31}P hyperfine splittings of 11−12 G (R = Me, *n*-Pr, *n*-Bu) and 8 G (R = Ph), with ^1H splittings of 2.2−2.4 G (α-alkyl; R = *n*-Pr, *n*-Bu), 0.2−0.3 G (β-alkyl; R = *n*-Pr, *n*-Bu), 2 G (*o*- and *p*-phenyl; R = Ph), and 0.8 G (*m*-phenyl; R = Ph).[8,9] Li^7-induced splitting is absent from these spectra. The 33 major peaks in the ESR spectrum of a freshly prepared solution of **4** can therefore be assigned to hyperfine splitting by the *m*-hydrogen atoms of a phenyl group, that is, $a_{m(1)} = 0.75$ G. The triplets into which each of the major peaks are split arise from splittings by the protons on the β-carbon of the 1,2-ethano group ($a_{\beta-\mathrm{alkyl}} = 0.25$ G). Because the 33 triplets are equally spaced, the splittings induced by the remaining atoms are multiples of 0.75 G. The monomodal intensity distribution of the peaks suggests overlapping between the outermost resonances of adjacent triplets created by the *m*-phenyl H atoms. Thus, the hyperfine splittings caused by either the *o*- or *p*-hydrogen atoms of the phenyl group having the most radical character, or by the α H atoms of the bridging 1,2-ethano group, are 1.5 G. In the absence of detailed experiments, which were beyond the scope of this investigation, it was not possible to establish the *a* values for these and the other atoms because the ^{31}P hyperfine splittings could not be determined by simple inspection (as was the case in previous work[8,9]). Iterative simulations using likely *a* values in the radical $PhP(Li)CH_2CH_2(Ph)P^{2-\bullet}(Li^+)_2$ produced spectra that closely resembled the one reproduced in Figure 1, however. By contrast, the spectrum in Figure 1 cannot be due to $Ph^{2-\bullet}(Li^+)_2$ or $Ph_2P^{2-\bullet}(Li^+)_2$.

Hydrolysis of 4. It has been reported that PhLi decomposes in THF with a half-life of ca. 12 h at 25 °C and 45 min at 65 °C.[16] Thus, boiling of a solution of freshly prepared **4** in THF for 2−3 h should have been sufficient to decompose PhLi, leaving **4** for protonation to **1**.[5]

The hydrolysis of a solution of **4** was not straightforward, however. The dropwise addition of water to a

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solution of **4** at 20 °C produced a mixture containing **5** (10−50%) and **1** (50−90%), according to NMR spectroscopy. When the hydrolysis was performed at 40 °C, **5** was produced in greater quantities (>40%). When carried out at 0 °C, the reaction afforded **1** in quantitative yield. Thus, the bis(phosphide) **4** is converted into the bis(secondary phosphine) **1** in high yield at ca. 0 °C. At higher temperatures, increasing amounts of **4** were converted into **5**. Similar results were obtained when the solution of **4** in THF was allowed to stand for 24 h prior to hydrolysis.

Hydrolysis of 4 in the Absence of PhP(Li)-$CH_2CH_2(Ph)P^{2-\bullet}(Li^+)_2$. The influence of the species absorbing at 421 nm in the hydrolysis reaction was investigated by observing the reaction of water with a solution of **4**·4THF in THF. When **4**·4THF was dissolved in THF, the solution exhibited an absorption at 366 nm. This solution produced pure **1** when treated with water, regardless of the reaction temperature (0, 20, 40 °C). The addition of 2−4 equiv of PhLi to the solution immediately prior to hydrolysis did not affect the outcome (the concentrations of the PhLi-containing solutions employed in these experiments were determined prior to use).[17]

From these observations it was concluded that the species displaying the absorption at 421 nm was responsible for the rearrangement leading to **5** when solutions of **4**, generated in situ, were hydrolyzed at >0 °C.

Cleavage of 2·2BH$_3$. The adduct **2**·2BH$_3$ was prepared by heating **2** under reflux with 4 equiv of $BH_3.SMe_2$ in THF.[18] The adduct was isolated as an air-stable, microcrystalline solid by evaporation of the solvent and chromatography of the residue on silica with dichloromethane as eluant. Characterizations of the product by $^{31}P\{^1H\}$ NMR (CDCl$_3$, δ 19.0) and ^1H NMR (CDCl$_3$, δ 7.8−7.3 (m, 20 H, ArH), 2.38 (d, 4 H, CH), 0.72 (br s, 6H, BH)) spectroscopy and electrospray mass spectrometry were consistent with the formulation **2**·2BH$_3$.

No reaction was observed when a mixture of **2**·2BH$_3$ in boiling THF (0.2 M) and lithium (10-fold excess) was stirred for 1 h, followed by a further 12 h at room temperature. Thus, **2**·2BH$_3$ is considerably less reactive toward lithium than **2**.

Influence of Impurities. To investigate the effect of sodium impurities in the lithium employed (99.9% lithium wire containing 0.01% sodium), experiments were performed using lithium pieces (98% Li containing 0.5−1.0% sodium) and lithium dispersion in mineral oil (99.95% Li). No notable changes in product yields or induction times were observed.

Summary. The cleavage of **2** by lithium in THF is dependent on temperature during the initial P−C bond cleavage and the later protonation step. An equilibrium appears to exist between the products of P−C$_{aryl}$ cleavage and those of P−C$_{alkyl}$ cleavage in these steps (Scheme 2); pathway I is relatively favored at 40 °C, and pathway II predominates at 0 °C. Thus, by performing the cleavage at 0 °C, P−C$_{alkyl}$ cleavage is minimized and the yield of **1** increased.

The products of the cleavage, lithium diphenylphosphide (**3**) and the bis(phosphide) **4**, are stable to heat, however. The major side-product of the reaction, PhLi, also appears to be more stable in THF in the presence of **4**. Alone, it forms a dimer that slowly reacts with THF.[19]

The addition of water to a solution of **4** in THF causes a reequilibration of the P−C$_{aryl}$ and P−C$_{alkyl}$ cleavage products as indicated by the dramatic changes in the proportions of products **1** and **5** at different reaction temperatures. Thus, **5**, which usually arises by pathway I, can be obtained from **4** of pathway II if the hydrolysis is carried out at elevated temperatures. The species present in the reestablished equilibrium are the same as those formed in the original cleavage reaction, because in both cases pathway II is favored at 0 °C, pathway I is favored at 40 °C, and pathways I and II are favored at 20 °C. The temperature dependence of this equilibrium indicates it to be thermodynamic in nature. It appears that the compound responsible for the reestablishment of the equilibrium is derived from the reaction of the red species (λ_{max} 421 nm) with water, because **1** is formed when water is added to a solution of PhLi and **4** at 40 °C, but **5** is formed in the presence of the red species. The ESR and UV−visible data, in conjunction with data from related systems, indicate that the red species is the radical anion $PhP(Li)CH_2CH_2(Ph)P^{2-\bullet}(Li^+)_2$, **7**. In common with other radical anions,[20] **7** will be a powerful reducing agent and readily protonated by water. The most likely product of the hydrolysis of **7**, and the only one that could reestablish the cleavage equilibrium, is the phosphinyl radical $PhP(Li)CH_2CH_2(Ph)P^\bullet$, which would be formed in a two-electron transfer from **7** to water (eq 5). One-electron transfer from **7** would produce $H^\bullet$ and **4**, the latter already being present in the reaction mixture and known to be unaffected by temperature. Direct abstraction of H^+ from water by **7** would produce $PhP(Li)CH_2CH_2(Ph)PH^{-\bullet}$ (Li^+) or $PhP(H)CH_2CH_2(Ph)PH^{-\bullet}(Li^+)$ and OH^-; none of these species could have been present in the initial cleavage equilibrium, and subsequent oxidation of the phosphinyl radical would lead directly to the desired product **1** without reestablishment of the equilibrium. Thus, the reaction of **7** with water releases $PhP(Li)CH_2CH_2(Ph)P^\bullet$, which reestablishes the cleavage equilibrium before final protonation by water to give secondary phosphines **1** and/or **5**. Accordingly, the phosphinyl radical must also have participated in the original cleavage reaction and equilibration of P−C$_{aryl}$ and P−C$_{alkyl}$ products.

It has been suggested[7] that small amounts of short-lived $Ph^{2-\bullet}(Li^+)_2$ may be generated from PhLi and lithium in tertiary phosphine−lithium mixtures; in this case the $Ph^\bullet$ radicals produced during hydrolysis would reestablish the equilibrium. The alternative products, PhLi (one-electron reduction) or $(C_6H_6)^{-\bullet}$ Li^+ (protonation), cannot reestablish the equilibrium.

This rationalization supports the assertion[7] that a number of steps are involved in the cleavage of tertiary phosphines by lithium. In particular, it is suggested that the initial reaction in the cleavage of **2** involves the phosphinyl radical $PhP(Li)CH_2CH_2(Ph)P^\bullet$ in addition to, or instead of, $Ph^\bullet$.

Mechanism. On the basis of these observations, a mechanism can be proposed for the lithium-induced cleavage of **2** in THF. The cleavage step comprises the

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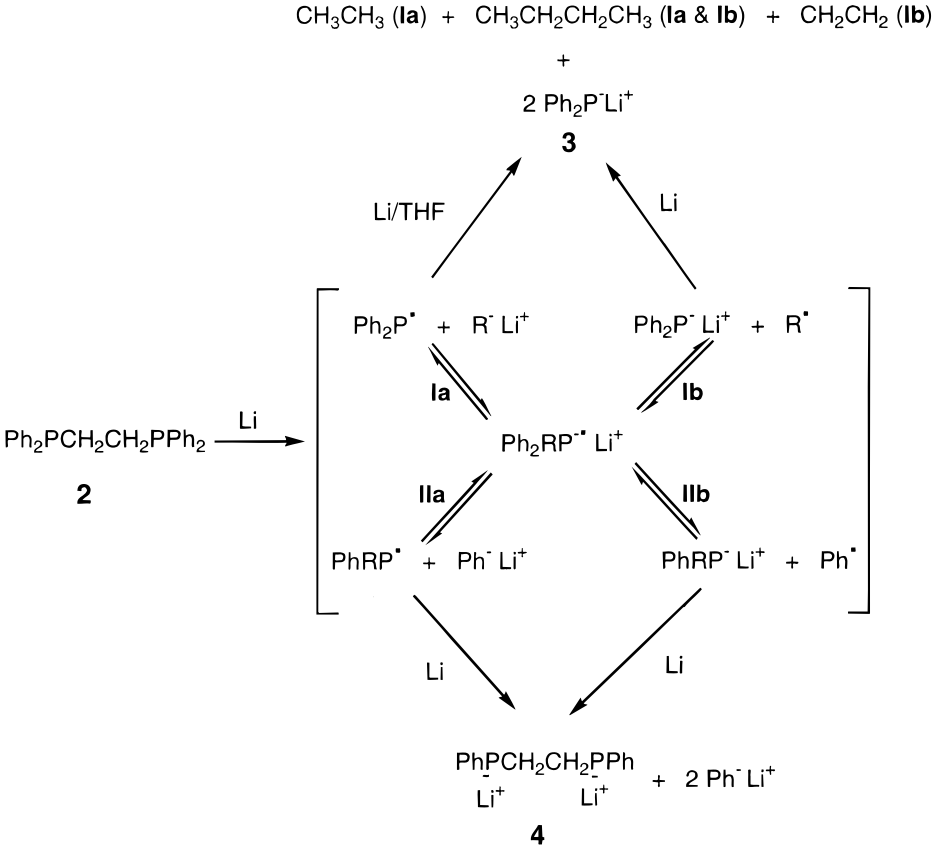
[20] For information on reductive electron transfer and proton abstraction by radical anions, see: Holy, N. L. *Chem. Rev.* **1974**, *74*, 243 and references therein.

Scheme 3



(R = $CH_2CH_2(Ph)P^-Li^+$ or $CH_2CH_2(Ph)P^{\bullet}$ (pathways **I**, **II** and central species) or $CH_2\text{-}CH_2^-Li^+$, $CH_2\text{-}CH_2^{\bullet}$ (pathway **I** only)

establishment of an equilibrium involving phosphinyl and phenyl/alkyl radicals and anions, followed by the irreversible formation of lithium phosphides. Scheme 3 summarizes the process, with the equilibria in the center of the scheme representing the processes occurring at each P atom.

When the lithium cleavage is performed at 0 °C, pathways IIa and IIb are possible for each P center. Our data indicates IIa as the pathway for the reestablishment of the cleavage equilibrium during hydrolysis.

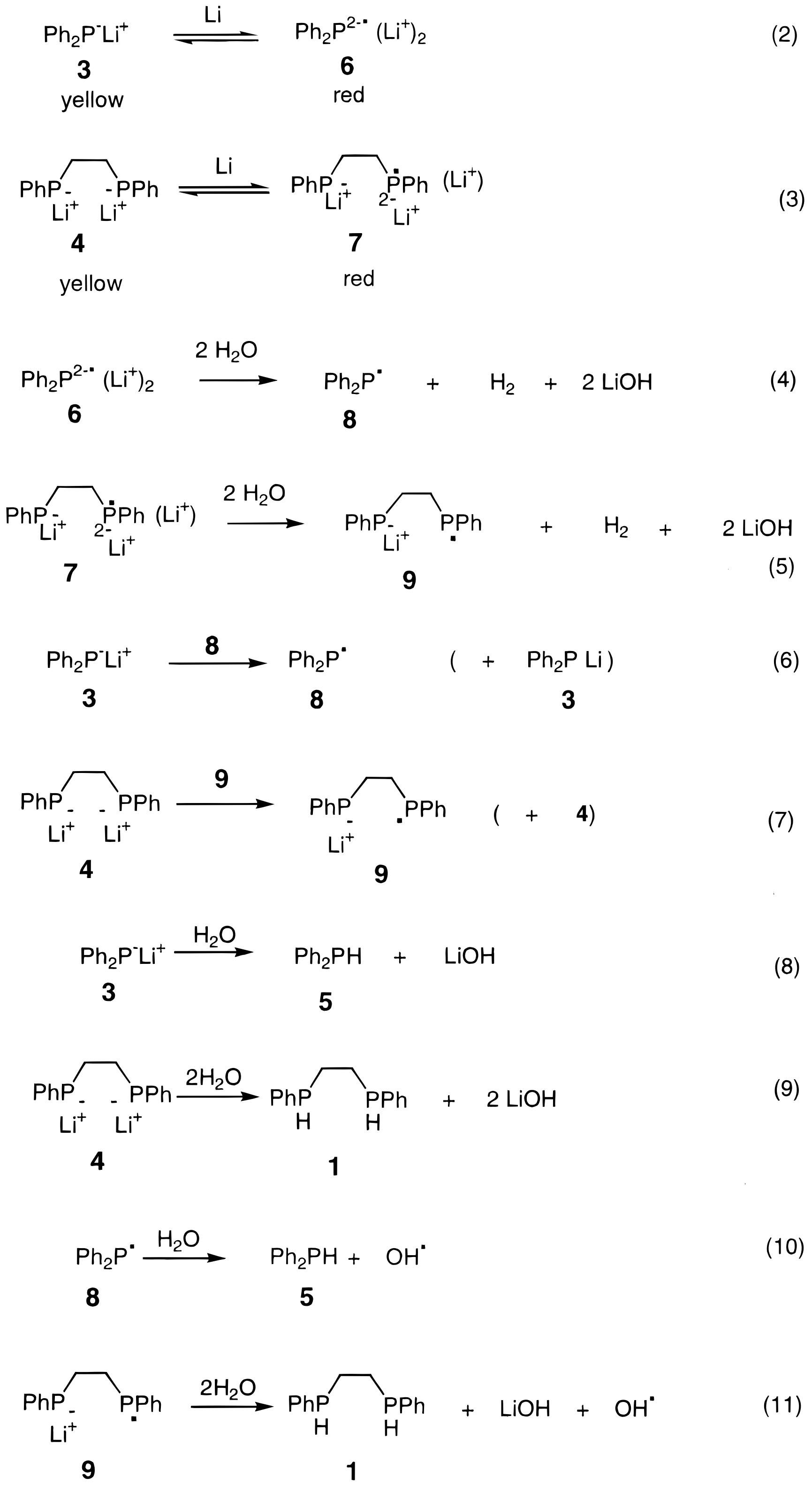
When the reaction is performed at more elevated temperature, pathways Ia and Ib are also possible for each P center. Each of these options produces different byproducts. If both P centers form phosphinyl radicals (pathway Ia) in the cleavage, the byproduct $LiCH_2CH_2$-Li will abstract $2H^+$ from solvent molecules to give CH_3-CH_3 (as observed in the cleavage of $Ph_2PCH_2PPh_2$ by lithium[7]). If one P center forms a radical (pathway Ia) and the other a phosphide ion (pathway Ib) during the cleavage, $LiCH_2CH_2^{\bullet}$ will be produced. This species may form $CH_3CH_2CH_2CH_3$ by dimerization and reaction with solvent molecules. If both P centers form phosphide ions (pathway Ib), the $^{\bullet}CH_2CH_2^{\bullet}$ generated will be liberated as ethylene. Ethylene has, in fact, been observed as a byproduct in the reaction, so Ib appears to be an important pathway.[7] However, because the cleavage involves a thermodynamic equilibria, pathway Ia must also be possible.[7]

When lithium reacts with **2** in THF at 20 °C, pathway Ib (and possibly Ia) therefore competes with pathway IIa and/or IIb. Following the irreversible formation of the bis(phosphide) **4** and/or mono(phosphide) **3**, it is clear that these species undergo further reaction with lithium to form the radical dianions **7** and **6**, respectively (eqs 2 and 3),[8,9] with which they are in equilibrium (Scheme 4). Neither process can alter the proportions of **3** and **4** already present in solution, nor can the presence of $Ph^{2-\bullet}(Li^+)_2$ or $Ph^{\bullet}$. These data are therefore consistent with the observation that the proportions of the phosphides **3** and **4** formed in the initial reaction are unaffected by subsequent changes in temperature.

The addition of water to the reaction mixture results in the formation of $Ph_2P^{\bullet}$, **8**, and/or $PhP(Li)CH_2CH_2PPh^{\bullet}$, **9**, as shown in eqs 4 and 5, and perhaps $Ph^{\bullet}$ from the hypothetical $Ph^{2-\bullet}(Li^+)_2$.[20] These species reestablish the cleavage equilibrium, which is shown in the central bracket of Scheme 3. Although the equilibrium applies to a small proportion of the phosphines in solution, its products are unstable and highly reactive. In the absence of lithium with which to form the more stable lithium phosphides, the reestablishment of the cleavage equilibrium occurs by a series of rapid intermolecular exchange reactions (eqs 6 and 7). The proportions of **3** and **4** in the solution readjust according to the populations of the species included in the cleavage equilibrium at the temperature at which the initial water is added. Further addition of water results in secondary phosphines (eqs 8−11).

A mechanism involving competitive release of a leaving group as the thermodynamically most-stable radical or

Scheme 4



anion also explains the incidence of P–C$_{alkyl}$ vs P–C$_{aryl}$ cleavage in the reactions of $Ph_2P(CH_2)_nPPh_2$ ($n = 1-5$) with lithium.[7] The leaving group can then separate as the alkyl radical when $n = 1$ but as the phenyl anion when $n = 3-5$. The nature of the bond cleavage therefore does not depend on leaving group preferences as radicals OR anions but rather on the relative thermodynamic stabilities of the radical and anionic species involved.

Conclusions

The cleavage of 1,2-bis(diphenylphosphino)ethane by lithium in THF involves a rapid equilibrium between P–C$_{aryl}$ and P–C$_{alkyl}$ cleaved anions and radicals, followed by their reaction with lithium and stabilization as lithium salts. The temperature dependence of the cleavage indicates that the equilibrium is thermodynamic in nature. The addition of water causes a reestablishment of the cleavage equilibrium prior to formation of the secondary phosphines with further water. The data collected in this investigation suggest a mechanism involving competitive separation of the leaving groups as the thermodynamically most-stable radical or anion. This mechanism is consistent with previous investigations involving homologous bis(tertiary phosphines).

Experimental Section

All reactions and manipulations were performed under an inert atmosphere using the Schlenk technique. THF was distilled off sodium/benzophenone ketyl. $^{31}P\{^1H\}$ NMR spectra were recorded at 20 °C on a Varian VXR 300S spectrometer operating at 299.96 MHz and referenced to external aqueous H_3PO_4 (85%). UV−visible spectra were obtained using a Cary 5E spectrometer and ESR spectra on a Bruker ER 200 D-SRC spectrometer. 1,2-Bis(diphenylphosphino)ethane, lithium wire (99.9%; sodium content ca. 0.01%), PhLi (1.8 M in diethyl ether/cyclohexane), and $BH_3{\cdot}SMe_2$ were purchased from Aldrich. Lithium diphenylphosphide and diphenylphosphine were prepared by literature methods,[5] as were $PhP(Li)(CH_2)_2P(Li)Ph$ and $PhP(H)(CH_2)_2P(H)Ph$.[13]

(*R, *R**)-(±)/(*R**, *S**)-1,2-Bis(phenylphosphino)ethane (1).** A mixture of finely divided lithium wire (13.8 g; 2 mol) in THF (360 mL) was cooled to 0 °C and vigorously stirred as a solution of 1,2-bis(diphenylphosphino)ethane (80 g; 0.2 mol) in THF (480 mL) was added over 4 h. After completion of the addition, the mixture contained crystals of **4**·4THF. The reaction mixture was warmed to room temperature and heated under reflux for 2 h. The hot solution was separated from excess lithium with use of a cannula and cooled to 0 °C over 1 h. The mixture was then stirred vigorously as aqueous THF (20% water, 50 mL) was added over 1 h. The brown reaction mixture was decolorized by the aqueous THF, and lithium hydroxide was deposited. The THF was removed in vacuo, and water (400 mL) and diethyl ether (200 mL) were added to the residue. Three extractions of the aqueous phase with similar quantities of diethyl ether followed. The combined extracts were dried ($MgSO_4$), filtered, and evaporated in vacuo to afford the product as a pale yellow, air-sensitive oil that was pure according to $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. The product distilled as a colorless oil having bp 140 °C (0.07 mmHg) [lit.[13] 140 °C; 0.07 mmHg]; 40 g (81% yield). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −46.43, −46.59 (*R**, *R**-(±)/*R**, *S**). ^1H NMR (C_6D_6): δ 1.80−2.10 (br m, 4 H, CH_2), 3.94 (br m, 1 H, PH), 4.62 (br m, 1 H, PH), 7.27 (br m, 6 H, ArH), 7.48 (br m, 4 H, ArH).

Acknowledgment. G.F.S., J.D., and J.B.S. thank the Australian Research Council for support of this work.

JO9907336