

Theoretical Study of the Reaction of Alkylolithium with Pyridylphosphines

Peter H. M. Budzelaar

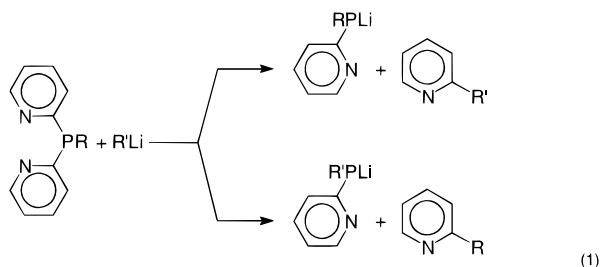
Department of Inorganic Chemistry, University of Nijmegen, Toernooiveld 1,
6525 ED Nijmegen, The Netherlands

Received August 29, 1997

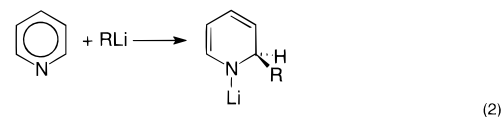
The reaction of pyridylphosphines with alkylolithium reagents has been investigated using *ab initio* methods. In earlier experimental studies, it was found that reaction of RLi with R'Py₂ produced a mixture of RPy, R'Py, (R)(Py)PLi, and (R')(Py)PLi; the reaction was assumed to involve "reductive elimination" from an (R)(R')(Py)₂P⁻Li⁺ intermediate. Our calculations show that the R for R' exchange does indeed involve such a species, although it is a transition state rather than an intermediate. Formation of phosphide, however, proceeds by direct attack of the alkylolithium on carbon C2 of a pyridyl group and is more properly designated as a nucleophilic substitution at carbon. Coordination of the pyridyl groups to lithium appears to be important in both reactions.

Introduction

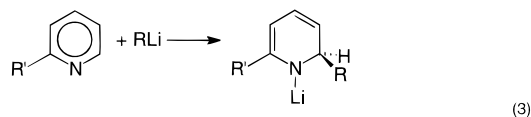
Phosphines are among the most versatile ligands used in homogeneous catalysis. Pyridylphosphines, which contain two donor atoms of very different coordination properties, give rise to a fascinating array of coordination geometries and several catalytic applications.¹ Palladium complexes of pyridylphosphines, in particular, are highly active in the alkoxy-carbonylation of acetylenes (MMA process).² We have previously reported the use of pyridylphosphines as building blocks for dinucleating ligands.³ During the synthesis of these ligands, we encountered a curious and unexpected reaction of organolithium compounds with di- and tripyridylphosphines, leading to lithium phosphides and α -substituted pyridines (eq 1).⁴



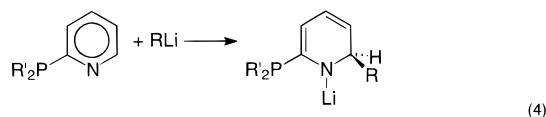
Normally, alkyl- and aryl-substituted phosphines do not react easily with organolithium compounds.⁵ Organolithium compounds add to pyridine derivatives to form dihydropyridyl derivatives (eq 2).⁶



This reaction has been known for a long time and has a certain preparative value.⁷ In the case of α -substituted pyridines, addition is normally directed toward the unsubstituted α -carbon atom (eq 3).



With phosphines bearing only a *single* pyridyl group, the expected product of addition to the pyridyl ring was indeed obtained (eq 4).



The unusual formation of phosphides from di- and tripyridylphosphines according to eq 1 was found to be rapid even at -80 °C in THF. At the time, we assumed the existence of a marginally stable intermediate (R)(R')(Py)₂P⁻Li⁺, which could exchange R groups or decompose by some kind of "reductive elimination" or C–C coupling to the observed products; this would explain the crossover of R and R' groups in eq 1. The group of Oae has repeated this work and moreover extended it to benzothiazoles; they proposed the same mechanism for the reaction.⁸ The assumption of a

* Corresponding author. tel (+31) 24 3652186. fax (+31) 24 3553450. email budz@sci.kun.nl.

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phosphoranide anion intermediate seems reasonable, because the isoelectronic sulfurane Ph_4S decomposes by a similar coupling reaction to Ph_2S and Ph_2 .⁹ Facile elimination of pyridyl groups has also been observed in sulfones,¹⁰ sulfoxides,¹¹ phosphonium salts,¹² and phosphinoxides.^{12,13} The general subject of "reductive elimination" or "ligand coupling" in hypervalent compounds has been reviewed.¹⁴

In transition-metal chemistry, the term "reductive elimination" is mostly used to indicate a process where two alkyl (or similar) groups leave the metal and combine in a more or less symmetric mechanism (eq 5). In the case of the main-group hypervalent compounds discussed here, the term is used to indicate the overall reaction, without implying a particular geometry of the transition state.



Although the assumption of a phosphoranide intermediate seems reasonable, it can explain neither the easy reaction of *pyridylphosphines* with alkyllithiums (*phenylphosphines* are not reactive under these conditions) nor the difference in behavior between mono- and dipyridylphosphines. Therefore, we decided to use theoretical methods to obtain insight into the unique reactivity of pyridylphosphines. In the present work, we will describe the results of a study on the model system $\text{MeLi} + \text{MePPy}_2$, which show that the postulated $(\text{R})_4\text{P}^- \text{Li}^+$ species are not on the path for C–C coupling, although they do play a role in exchange of organic groups at phosphorus.

Methods

All calculations were of the all-electron closed-shell restricted Hartree–Fock type, and were carried out using the GAMESS program.¹⁵ Structures were fully optimized (as minima or transition states) at the RHF/3-21G(*)¹⁶ level, and single-point calculations at the RHF/3-21G(*) geometries were then carried out at the RHF/6-31G*¹⁷ and MP2/6-31G* levels. To check the importance of correlation effects on geometries, transition states **3a**, **3b**, **4a** and **4d** were reoptimized at the MP2/3-21G(*) level. This was found to affect mainly the

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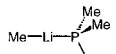
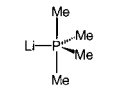
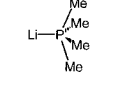
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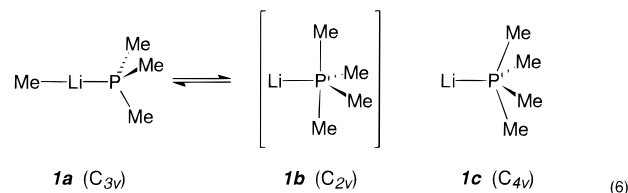
Table 1. Total and Relative MP2/6-31G*//RHF/3-21G(*) Energies for the $\text{MeLi}\cdot\text{PMe}_3$ System

Molecule	E (a.u.)	E _{rel} (kcal/mol)
 1a minimum	-507.29232	(0)
 1b transition state	-507.22348	+42.2
 1c 2 nd order saddle point	-507.20901	+51.3

geometry of the pyridyl ring; changes to the positions of the atoms involved in the reaction were minimal, as were changes to the final relative MP2/6-31G* energies. Structure drawings shown in the text were prepared using the PLUTO program.¹⁸ Tables 1–5 contain total and relative energies at MP2/6-31G*//RHF/3-21G(*) energies at lower levels are given in the Supporting Information (Tables S6–S10).

Results and Discussion

Alkyl Exchange and Reductive Elimination in the $\text{MeLi} + \text{PMe}_3$ System. As a model for "typical" $(\text{R})_4\text{P}^- \text{Li}^+$ species, we briefly investigated the system $\text{MeLi} + \text{PMe}_3$ (Table 1). The most stable structure is the σ -complex $\text{MeLi}\cdot\text{PMe}_3$ **1a**. A trigonal-bipyramidal structure of Me_4PLi (**1b**) with two long and two short P–C bonds was found to be a transition state for methyl exchange at phosphorus; the square-pyramidal structure **1c** with four equivalent P–C bonds is a second-order saddle point.



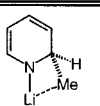
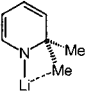
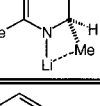
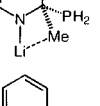
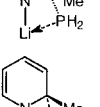
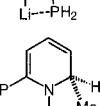
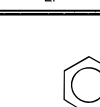
The potential-energy surface is rather flat in this region, and details may change with a different choice of basis set or with optimization at correlated levels. However, the calculated activation energy for methyl exchange (42 kcal/mol) clearly indicates that this is *not* an easy reaction, in accord with experimental observations. More importantly, we could not locate a transition state for the C–C coupling (ethane formation) in this system. Again, this agrees with experimental observations (the normal reaction is metalation of a methyl group), but it also demonstrates that pyridylphosphines (where "elimination" is already fast at -80°C) are for some reason very special.

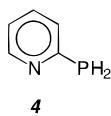
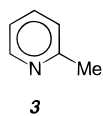
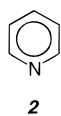
Reactions of MeLi with Pyridines. To investigate this "special character", we looked at possible reactions of MeLi with pyridine (**2**), 2-methylpyridine (**3**), and 2-phosphinopyridine (**4**) (Table 2).

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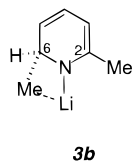
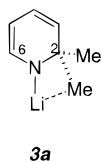
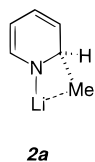
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Table 2. Total and Relative MP2/6-31G/RHF/3-21G(*) Energies for Addition of MeLi to Pyridines**

Molecule	E (a.u.)	E _{rel} (kcal/mol)
 2a TS	-294.67265	
 3a TS	-333.85195	-0.7
 3b TS	-333.85077	(0)
 4a TS	-636.09005	-2.8
 4b minimum	-636.12995	-27.9
 4c TS	-636.12572	-25.2
 4d TS	-636.08553	(0)

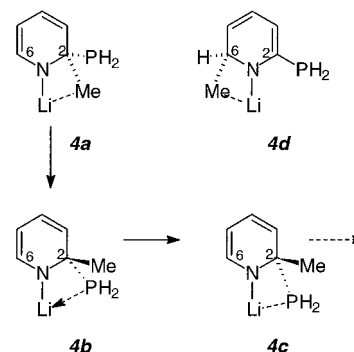


Coordination of pyridine to MeLi is quite strong. After complexation, 1,2-addition of the alkylolithium to the pyridine ring can occur, resulting in a dihydropyridyl-lithium complex via a normal 4-center transition state (**2a**). If there is a methyl group at the 2-position, addition can occur in a 1,2-fashion (transition state **3a**) or 1,6-fashion (**3b**). Our calculations indicate that the difference in activation energies is very small (0.7 kcal/mol in favor of 1,2-addition). Experimentally, 1,6-addition is usually observed, although side reactions such as metalation of the methyl group often compete.



In the reaction of MeLi with 2-phosphinopyridine, addition can again occur in a 1,2- or 1,6-fashion. The two transition states (**4a** and **4d**) are again found to be close in energy, 1,2-addition being favored by 2.8 kcal/mol (**4a**). Coordination of the phosphorus atom to Li favors 1,2-addition, but this interaction is rather weak (and will be negligible in the presence of coordinating solvents). Steric factors favor 1,6-addition. Obviously, there are no experimental data for this system (deprotonation of the phosphino group would occur instead); for

the more sterically hindered 2-(diphenylphosphino)pyridine our experimental results⁴ indicated a preference for 1,6-addition.



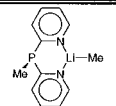
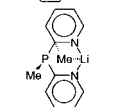
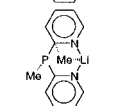
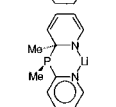
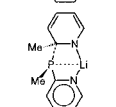
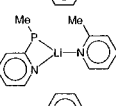
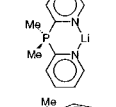
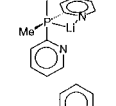
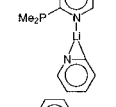
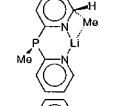
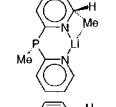
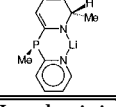
The 1,6-adduct is stable. The 1,2-adduct **4b**, however, is only a shallow minimum and easily decomposes with loss of phosphide to give the methylpyridine complex of lithium phosphide via transition state **4c** ($E_a \approx 3$ kcal/mol). This is the product of formal reductive elimination from (H)₂(Me)(Py)PLi, but here it is obtained by methyl attack at carbon, *not* at phosphorus. These results suggest that the same might be true for the di- and tripyridylphosphines studied experimentally.

Reaction of MeLi with MePPy₂. After the above preliminary investigations, we decided to study a more realistic model system, namely MeLi + MePPy₂ (Table 3). Experimentally, this has been found to give MePy + (Me)(Py)PLi in a clean and rapid reaction.⁴ Our model does not include association of the organolithium reagent (MeLi is a tetramer) or solvent (the reaction was usually carried out in THF or diethyl ether), but apart from that it represents the "real system". The reactions studied are summarized in Scheme 1.

The initial MeLi·Py₂PMe complex **5a** can undergo four distinct reactions. The first is degenerate methyl exchange via the trans ate complex **5g**, which is predicted to be easy ($E_a \approx 19$ kcal/mol). This reaction is much easier than alkyl exchange in "normal" alkyl- and arylphosphines as discussed earlier ($E_a > 40$ kcal/mol) because it is assisted by coordination of the pyridyl groups to lithium. The second reaction, exchange of a methyl group for a pyridyl group via the cis ate complex **5h**, leads to a more stable product, PyLi·PyPMe₂ (**5i**). However, this reaction is not so efficiently assisted by pyridyl coordination and has a much higher activation energy ($E_a \approx 29$ kcal/mol). Structures for these two substitution reactions are shown in Figure 1. Solvent effects are expected to stabilize the strongly charge-separated transition states **5g** and **5h** relative to the remaining addition transition states, but this point was not investigated further.

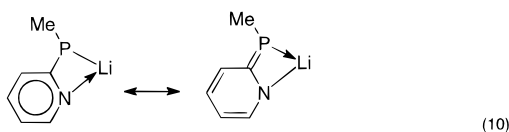
The third possibility is addition of the methyl group to carbon C2 of a pyridyl group (**5b**), leading to dihydropyridyl derivative **5d** which immediately decomposes to the phosphide (Me)(Py)PLi·PyMe **5f**. This reaction has an activation energy ($E_a \approx 19$ kcal/mol) that is close to the Me for Me exchange, but lower than the Me for Py exchange. Its final product is very stable because the negative charge on the phosphide is delocalized to the pyridyl ring (eq 10). This is reflected in the bond lengths within the pyridyl ring (Figure 2) and in the NMR parameters for this anion.⁴ X-ray structures of Py₂PLi(THF)₂ and Py₂PAlMe₂ show the presence of bis(nitrogen)

Table 3. Total and Relative MP2/6-31G*//RHF/3-21G(*) Energies for the MeLi·Py₂PMe System

Molecule	E (a.u.)	E _{rel} (kcal/mol)
 5a	-921.68648	(0)
minimum		
 5b	-921.65579	+19.3
TS		
 5c	-921.64987	+23.0
TS		
 5d	-921.69444	-5.0
minimum ^a		
 5e	-921.69781	-7.1
TS ^b		
 5f	-921.74056	-33.9
minimum		
 5g	-921.65541	+19.4
TS		
 5h	-921.63986	+29.2
TS		
 5i	-921.69390	-4.6
minimum		
 5j	-921.66246	+15.1
TS		
 5k	-921.65936	+17.0
TS		
 5l	-921.69655	-6.3
minimum		

^a Local minimum at RHF; probably not a stationary point at MP2. ^b Transition state at RHF; probably not a stationary point at MP2.

chelation and no metal–phosphorus coordination,¹⁹ demonstrating the importance of this type of resonance in pyridylphosphides.



Finally, MeLi can add in a 1,6-fashion (**5j**), giving an internally coordinated addition product **5l** which will not

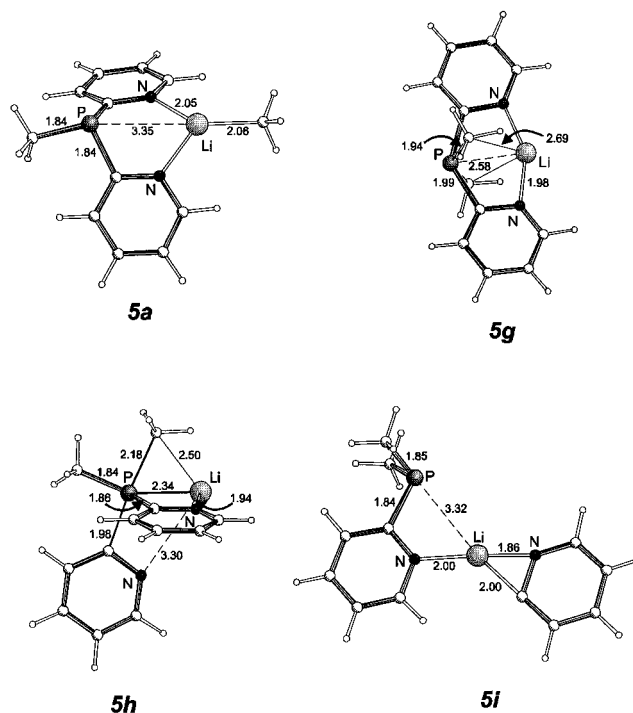


Figure 1. Nucleophilic substitution at phosphorus in the MeLi+Py₂PMe system: MeLi·Py₂PMe adduct (**5a**), methyl exchange TS (**5g**), Me-Py exchange TS (**5h**) and PyLi·PyPMe₂ (**5i**).

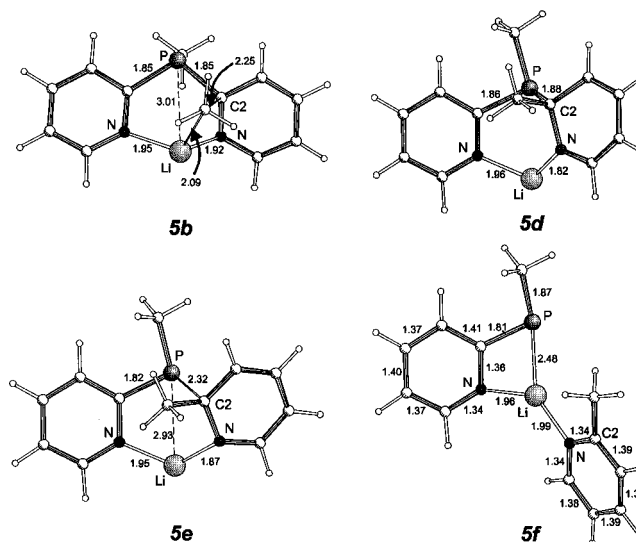
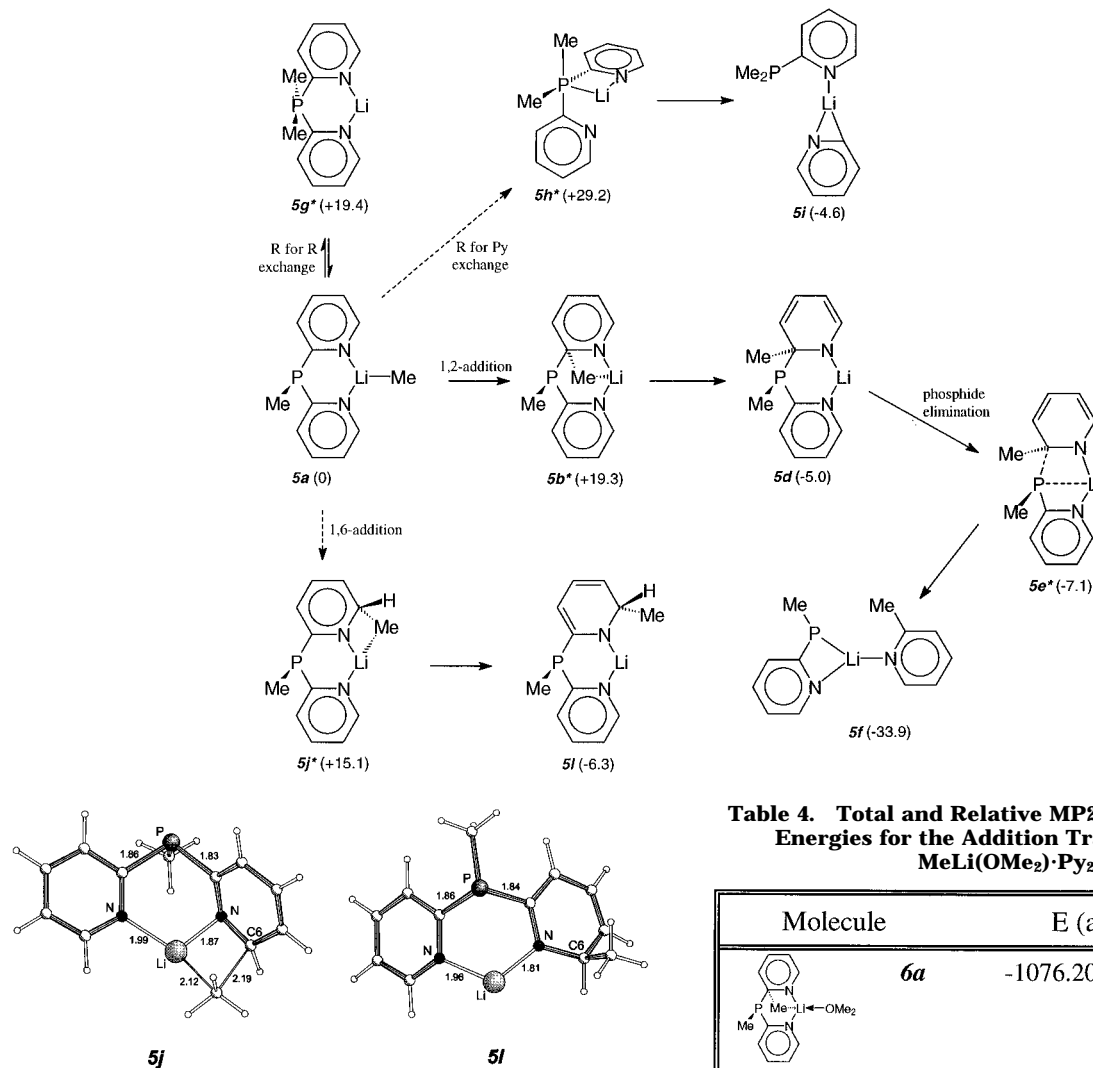
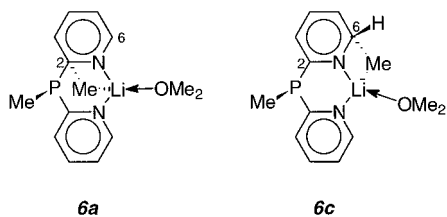


Figure 2. C–C coupling through addition–elimination in the MeLi+Py₂PMe system: 1,2-addition TS (**5b**), 1,2-adduct (**5d**), phosphide elimination TS (**5e**), and lithium phosphide–pyridine complex (**5f**).

react further (Figure 3). According to our calculations on the simple model system, 1,6-addition should be somewhat *easier* than 1,2-addition (by ≈ 4 kcal/mol), in contrast with experimental observations. It occurred to us that solvation might influence the balance between the two modes of addition. Indeed, calculations on a model containing a single molecule of dimethyl ether (Table 4) result in a decrease of the preference for 1,6-addition to only 1.6 kcal/mol. Thus, solvation favors 1,2-addition over 1,6-addition, but—at least at the MP2/6-31G*//RHF/3-21G(*) level—not by enough to predict the correct outcome of the experiment. Dimethyl ether is a

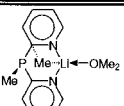
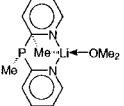
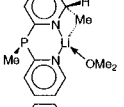
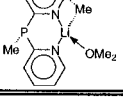
Scheme 1. Summary of Reactions in the MeLi·Py₂PMe System (relative energies in kcal/mol). Species Marked with a * Are Transition States at RHF/3-21G(*)**Figure 3.** 1,6-addition of MeLi to MePPy₂: TS (**5j**) and product (**5i**).

weak donor, and a poor model for solvation and/or aggregation, but unfortunately we cannot do better for these large systems. The reason solvation has this effect is easy to understand. In the 1,2-addition transition state **5b**, all atoms coordinated to Li are on one side of the metal atom, leaving a large "hole" available for solvent coordination. In contrast, the 1,6-addition transition state **5j** has all donor atoms distributed around Li more evenly. This results in a stabilization of *unsolvated* **5j** relative to **5b**, and consequently in a *lower solvation energy* for **6c** than for **6a** (Figure 4). This problem does not occur in monopyridylphosphines, where the environment around Li is virtually identical for the two addition modes.



(11)

Table 4. Total and Relative MP2/6-31G*//RHF/3-21G(*) Energies for the Addition Transition States in MeLi(OMe₂)·Py₂PMe

Molecule	E (a.u.)	E _{rel} (kcal/mol)
	-1076.20457	+1.6
	-1076.19885	+5.2
	-1076.20720	(0)
	-1076.20590	+0.8

Organolithium reagents are always either solvated or associated to oligomers (or both). Thus, if solvation *can* have a significant effect on the addition, this effect will in practice always be observed.

To summarize, we find that there are three *separate* low-energy reaction pathways in this system:

A: Me exchange at phosphorus, via an Me₂PPy₂⁻ like transition state.

B1: Direct Me attack at pyridyl carbon C2, eventually leading to phosphide formation.

B2: Direct Me attack at pyridyl carbon C6, leading to a dihydropyridyl derivative.

Reaction A, which is responsible for the experimentally observed "crossover" of alkyl groups in eq 1, is strongly

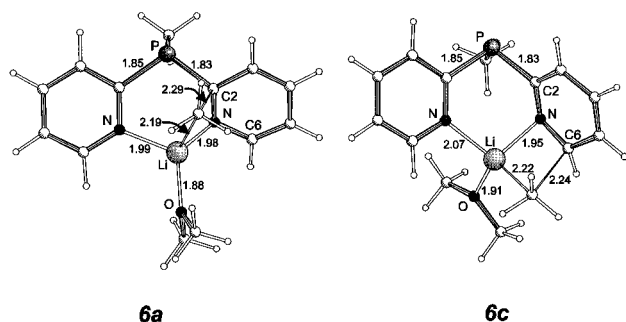


Figure 4. Solvated transition states for 1,2 (**6a**) and 1,6 (**6c**) addition of MeLi to MePPy₂.

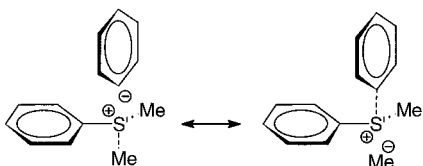
Table 5. Total and Relative MP2/6-31G*//RHF/3-21G(*) Energies for the SMe₂Ph₂ System

Molecule	E (a.u.)	E _{rel} (kcal/mol)
7a minimum	-938.83543	(0)
7b TS	-938.80891	+16.6

assisted by coordination of the two pyridyl groups to Li and will not occur in monopyridylphosphines. Reactions B1 and B2 are calculated to be close in energy. Experimentally, B1 is observed for di- and tripyridylphosphines, whereas we still calculate a small preference for B2. Higher-level theoretical methods and/or a better treatment of solvation might be required to get this right. For monopyridylphosphines, where geometric constraints caused by Li–N coordination are less important, B2 should always be preferred, in agreement with experiment.

Elimination from Sulfuranes and Other Hypervalent Compounds. As mentioned in the Introduction, sulfuranes can undergo an elimination that appears to be related to the C–C coupling we observed with pyridylphosphines. However, in the case of sulfuranes the reaction requires neither lithium coordination nor the presence of pyridyl groups. So, what is the relation—if any—between elimination from sulfuranes and from pyridylphosphines? To elucidate this, we have calculated the structure of *cis*-SMe₂Ph₂ (**7a**) and its elimination transition state (**7b**) (Table 5); bond lengths are shown in Figure 5.

The calculated structure of sulfurane **7a** is trigonal-bipyramidal with two long apical “half-bonds”, similar to the structure predicted by Marsden for Me₄S.²⁰ The apical groups bear a fairly large negative charge (≈−0.3 e each according to DMA²¹). A classical representation using two ionic resonance structures (eq 12) appears to have a significant contribution.



(12)

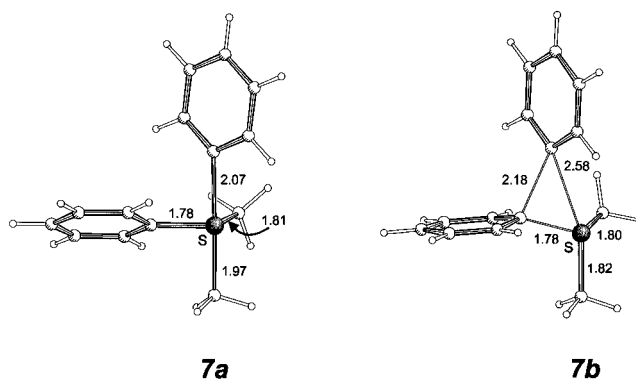


Figure 5. Structure of *cis*-SMe₂Ph₂ (**7a**) and its elimination TS (**7b**).

Transition state **7b** shows a much larger concentration of negative charge (≈−0.5 e) on the apical phenyl group. Also, the apical S–Ph bond has become very long (2.58 Å, from 2.07 Å in **7a**), whereas the equatorial S–Ph bond has not lengthened at all (1.78 Å in both **7a** and **7b**). Thus, the transition state appears to have a phenyl anion attacking the *ipso* carbon atom of the phenyl group of the SMe₂Ph⁺ sulfonium cation, and most of the activation energy seems to be needed for the localization of charge on one of the two apical substituents.

Our calculated activation energy (16.6 kcal/mol for SMe₂Ph₂) is reasonably close to the experimental one (10.6 kcal/mol for SPh₄). More importantly, Furukawa⁹ observed a large negative entropy of activation (−23.5 eu), which is surprising for such a unimolecular reaction. He carried out his reaction in THF, which has a sizable dipole moment. Since the calculated transition state has such a large charge separation, the reaction will be accompanied by significant solvent organization in a polar solvent, which can explain the large negative entropy of activation.

When we now compare this sulfurane system with the phosphines discussed in earlier sections, we can see similarities as well as differences:

The elimination mechanism follows a similar pathway in both cases: attack of a nearly anionic alkyl or aryl group on an *ipso* carbon atom. The mechanism does not resemble the nearly symmetric reductive elimination reactions commonly encountered in transition metal chemistry.

Pyridyl groups are required in the phosphine case, but not for sulfuranes. The most probable reason for this difference is that phosphides are not very good leaving groups, so that a rather reactive carbon atom is needed for attack. Thioethers, on the other hand, are very good leaving groups.

Trigonal bipyramidal species can be stable intermediates for sulfuranes, whereas the corresponding phosphorus compounds (R)₄P[−] Li⁺ are only transition states.

Conclusions

In his review of ligand coupling reactions of hypervalent species,¹⁴ Oae states that “Ligand coupling is a concerted reaction by orbital interaction between an axial and an equatorial ligand”. The present work shows that the coupling reaction is best described as an intramo-

(20) Marsden, C. J.; Smart, B. A. *Organometallics* **1995**, *14*, 5399.

(21) Stone, A. J. *Chem. Phys. Lett.* **1983**, *83*, 233.

lecular nucleophilic substitution involving a free or nearly free carbanion. In the case of the pyridylphosphines, the hypervalent species $(R)_4P^- Li^+$ is strictly speaking not even on the path for C–C coupling. Thus, C–C coupling is a very asymmetric process, and describing it as a concerted reaction is somewhat misleading.

Oae stresses the importance of the central atom in determining the ease of C–C coupling, but does not comment on the predominance of pyridyl examples in the literature. Our results indicate that pyridyl derivatives (and the benzothiazoles studied by Oae⁸) are special in that they allow easy C–C coupling through an addition–elimination mechanism. This allows coupling of pyridyl groups in cases where e.g. the corresponding phenyl systems would be unreactive. Ordinary alkyl and aryl groups only undergo coupling if the hypervalent species can form a very good leaving group, as in the case of sulfuranes.

The two possible modes of addition (1,2 and 1,6) are very close in energy, and the balance between the two is not predicted correctly even at MP2/6-31G**/RHF/3-21G(*); shortcomings of the theory and/or the choice of

the model system may be responsible for this. Both coordination and solvation seem to be important in directing the reaction either to simple 1,6-addition or to 1,2-addition followed by elimination. Coordination of pyridyl groups to lithium was also found to play a crucial role in promoting alkyl exchange. It seems plausible that coordination-assisted substitution at phosphorus is much more common than is generally assumed, and this could be exploited in the synthesis of new phosphines, e.g. for use as ligands.

Acknowledgment. We want to thank Dr. J. H. van Lenthe (University of Utrecht) for valuable discussions and generous grants of computer time.

Supporting Information Available: Tables S6–S10: Total and relative energies for species 1–7 at various levels of theory (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9716136