of the solvent. Under such conditions the reactions leading to hydration and adduct formation are not possible; Scheme II predicts the absence of a disparity between the measured kinetic and partitioning isotope effects, and no disparity is observed.[13] Similar arguments can be proposed for explaining the observed disparity in the reduction of *N*-methylacridium ion by *N*-alkyldihydronicotinamides.[14] The key to the argument is the extreme sensitivity of the equilibrium of adduct formation to the amount of water present and the well-known difficulty of preparing and maintaining totally anhydrous polar protic solvents like acetonitrile. Further support for Scheme II may be found in the reported reaction of *N*-alkylpyridines with sterically hindered oxidants carried out under conditions where the formation of hydration product and adduct would be unfavorable. For example, the reactions of thiopivalophenone,[1] benzoyl formate,[1] and hexachloroacetone[2] with *N*-benzyldihydronicotinamide, the reactions of 4-X-2,6-dinitrobenzenesulfonate with NADH,[15] and the reactions of π acceptors with *N*-methylacridan[16] show no disparity between the measured kinetic and partitioning isotope effects.

In summary, we have presented evidence that the course of the reaction of a dihydronicotinamide with a carbonyl is dependent on the steric bulk of the reactant and the reaction conditions. The observed products can be rationalized by a scheme that involves initial electron transfer. The observations have important implications with regard to the interpretation of the disparity between the measured kinetic and partitioning isotope effects in several reported NADH model systems.

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(11) k_{HH} and k_{HD} are the second-order rate constants for the disappearance of the diprotio- and monodeuterio-*N*-alkyldihydronicotinamides, respectively, in their reactions with substrate; k_H and k_D are the second-order rate constants associated with C-H and C-D bond cleavage, respectively, during the oxidation of the *N*-alkyldihydronicotinamide; k_{hyd} and k_A are the second-order rate constants for the formation of hydration product of the dihydronicotinamide and 1:1 adduct, respectively.
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Direct Observation of the Monomeric Metaphosphate Anion

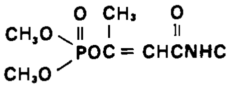
Sir:

We report herein the direct observation of the monomeric metaphosphate anion, PO_3^-.

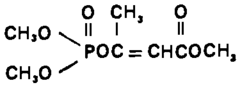
This species was first proposed in 1955[1] as an intermediate in hydrolysis of phosphomonoesters in aqueous solution. The hypothesis has since been extended to include other reactions and additional monomeric metaphosphate species as intermediates.[2] Recent work on phosphoryl transfer from aryl phosphates to alcohols and water in largely aprotic media has provided substantial evidence for the intermediacy of the monomeric metaphosphate anion.[3] Despite widespread acceptance of the concept, not until 1974 was the first unequivocal experimental evidence reported for the preparation of any monomeric metaphosphate, specifically the methyl ester in the vapor phase.[4] Subsequently, two of us and associates demonstrated the formation of a number of monomeric metaphosphate species via both thermal and electron-impact-induced reactions in the mass spectrometer, in part from our own work but largely on the basis of published data in an extensive preexisting literature on mass spectrometry of organophosphorus compounds.[5,6] Despite the passage of nearly 25 years since the original proposal, however, the monomeric metaphosphate anion has continued, understandably, to evoke references to an "evanescent"[7] or "mythical"[8] intermediate.

Some of us recently reported mass spectra, measured by a variety of experimental techniques, of several organophosphorus pesticides.[9] Negative-ion chemical-ionization[10] spectra of some of these compounds contained prominent peaks at *m/z* 79. In this context, such a peak would have to be attributed to either PO_3^- or $CH_4PO_2^-$. The precise masses of these species, 78.9585 and 78.9949, respectively, differ by 0.0364 u, enough to allow easy differentiation by high-resolution mass measurement. We have now made such measurements on the four pesticides whose structures are displayed. The results, listed in Table I, leave no doubt that we have observed the monomeric metaphosphate anion.[11]

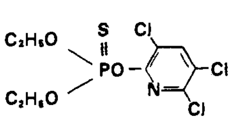
The remaining 0.1% of intensity at *m/z* 79 in the spectra of Monocrotophos and Mevinphos appears to be attributable to $CH_4PO_2^-$. The remaining ~10% in Azinphos methyl appeared



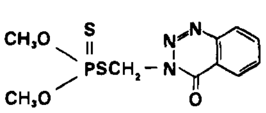
Monocrotophos



Mevinphos



Dursban



Azinphos Methyl

Table I. Precise Mass Measurements on Peaks at *m/z* 79 in Negative-Ion Chemical-Ionization Spectra

compd	measd mass	assignment ion	assignment mass	% of total ion current at *m/z* 79
Monocrotophos	78.9590	PO_3^-	78.9585	99.9
Mevinphos	78.9590	PO_3^-	78.9585	99.9
Dursban	78.9590	PO_3^-	78.9585	80
	78.9446	PSO^-	78.9407	20
Azinphos methyl	78.9409	PSO^-	78.9407	~90

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as an unresolved shoulder on the PSO^- peak and its mass could not be measured accurately, but an estimate by visual interpolation indicates that it is almost certainly due to PO_3^-. Azinphos methyl contains only two phosphoryl oxygen atoms; hence it cannot produce a PO_3^- ion except by reaction with the moderator gas.

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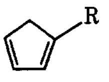
Synthesis of $(C_6H_5)_2PCH_2Si(CH_3)_2C_5H_4Li$: A Novel Heterodifunctional System for the Directed Linkage of Dissimilar Transition Metal Fragments

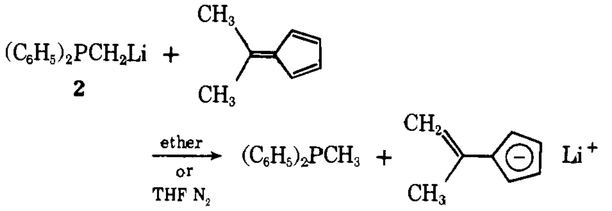
Sir:

Reports of interesting and often synthetically useful chemical processes carried out by two or more organometallic species in combination are becoming increasingly common.[1] The construction of model systems possessing two metals linked by ligand bridges, but not necessarily direct metal–metal bonds, is one approach toward probing the chemical interactions between these metal centers. Ligand bridges possessing pairs of trisubstituted phosphines (or other group 5 analogues) are of course well known;[2] far less common are reports of linked cyclopentadienide rings.[3] Both general classes of compounds are of value in the formation of bimetallic compounds possessing two identical metal centers but, not unexpectedly, are poorly suited for the construction of systems possessing very different types of metals, e.g., "early" and "late" transition metals in the same molecule. Much more versatile would be a linkage containing both phosphine and cyclopentadienide functionality. It is quite surprising, therefore, that only four such systems have been described (**1a–d**),[4] three having a direct phosphorus-ring bond, and *not a single example of such a ligand being synthesized, isolated, and attached to two different metals has ever been reported.*[5a] We report herein the initial results of our studies involving the synthesis of the first heterodifunctional compounds containing remote phosphine and cyclopentadienide functionality, and their application in the production of heterodinuclear organometallic complexes.

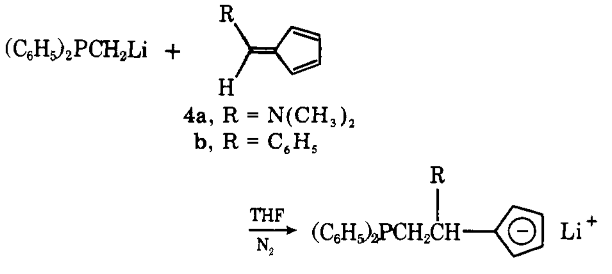


1a, $R = P(OR)_2$[4a]
b, $R = PF_2$[4b]
c, $R = P(C_6H_5)_2$[4c,d]
d, $R = CH_2P(C_6H_5)_2$[4e]

Both direct and stepwise routes to the desired ligands have been investigated. In the former category fall attempts to add phosphine-containing nucleophiles to fulvenes. The reaction of diphenylphosphinomethyllithium (**2**)[6] with dimethylfulvene in ether or THF leads, however, entirely to the products of proton transfer (eq 1). Although this result is not inherently surprising, it contrasts sharply with the large number of literature reports describing additions of aryl- and alkyllithiums to dimethylfulvene, none of which indicates the interference of the proton-transfer process.[7] Addition of **2** to fulvenes lacking acidic hydrogens (**4a and 4b**) does appear to take place (eq 2). In the case of **4a**, the reaction proceeds cleanly upon slow addition of solid **2**, but the product is extremely reactive and gives rise to complex chemistry when subjected to further organic transformations. The product of addition of **2** to **4b** does not form as cleanly, and, therefore, we have proceeded to develop the stepwise approach described in Scheme I.



(1)



4a, $R = N(CH_3)_2$
b, $R = C_6H_5$

(2)

Slow addition of a THF solution of **2** TMEDA[8] to a large excess of dichlorodimethylsilane in THF yields predominantly monoaddition product **6** if both solutions are held at −78 °C over the course of the addition. The products **5** and **6** are interesting spectroscopically because their NMR spectra display larger phosphorus–hydrogen four-bond (PCSiCH) coupling (J^4 = 0.9 and 0.7 Hz, respectively) than two-bond (PCH) coupling ($J^2 \leq 0.5$ Hz) in C_6D_6 solvent.[9,10] After removal of

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