

Kishner reduction of (\pm)-**33** (109 mg, 0.54 mmol) with 80% hydrazine hydrate (0.07 mL), KOH (40 mg), and triethylene glycol (1 mL) was carried out as described for the preparation of the (-) enantiomer. Chromatography afforded a solid which was sublimed at 50 °C (20 mm) to give **10**: 74 mg (73% yield); mp 100 °C (in a sealed tube) (lit.¹³ mp 100–102 °C).

Anal. Calcd for C₁₄H₂₀: C, 89.29; H, 10.71. Found: C, 89.22; H, 10.69.

Aluminum Bromide Catalyzed Isomerization of (\pm)-10**.** Aluminum bromide (150 mg) was added to a solution of (\pm)-**10** (50 mg, 0.266 mmol) in dry carbon disulfide (3 mL), and then the reaction mixture was stirred for 5 h at room temperature. The mixture was poured onto ice and was extracted with ether. The ethereal extract was washed with aqueous NaHCO₃ solution and water and dried (MgSO₄). Removal of the solvent gave a white

solid, whose GLC analysis (5% SE-30 packing) exhibited a single peak. The solid was chromatographed over neutral alumina (activity III), and elution with pentane gave diamantane (**42**): 47 mg (94% yield); mp 238–240 °C (in a sealed tube) (lit.^{22a} mp 236–237 °C, lit.^{22b} mp 244.0–245.4 °C); mass spectrum, *m/e* 188 (M⁺).

Anal. Calcd for C₁₄H₂₀: C, 89.29; H, 10.71. Found: C, 89.15; H, 10.54.

Registry No. (-)-**9**, 77122-03-3; (\pm)-**10**, 77079-50-6; (-)-**10**, 77122-04-4; (-)-**21**, 70209-48-2; (\pm)-**22**, 77079-51-7; (\pm)-**23**, 77122-05-5; (\pm)-**24**, 77079-52-8; (\pm)-**25**, 77122-06-6; (\pm)-**28**, 77122-78-2; (+)-**28**, 77079-53-9; (-)-**28**, 77122-79-3; (\pm)-**29**, 77079-54-0; (-)-**29**, 77122-07-7; (\pm)-**30**, 77079-55-1; (-)-**30**, 77122-08-8; (\pm)-**32**, 77079-56-2; (\pm)-**33**, 77079-57-3; (-)-**33**, 77122-09-9; (\pm)-**42**, 77079-58-4.

Reactions of [(Diphenylphosphino)methyl]lithium with Dimethylfulvene

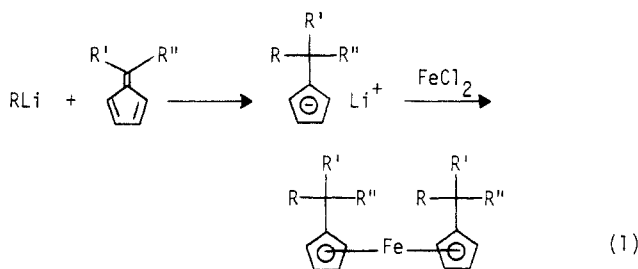
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[(Diphenylphosphino)methyl]lithium reacts with dimethylfulvene in ether or THF to yield exclusively lithium isopropenylcyclopentadienide, the product of proton transfer. Neither steric nor electronic effects alone appear sufficient to explain this anomalous result. A similar reaction in petroleum ether gives rise to three major products: lithium [1,1-dimethyl-2-(diphenylphosphino)ethyl]cyclopentadienide and the dilithium salts of 6-(1,3-cyclopentadienyl)-6,8,8-trimethylbicyclo[3.3.0]octa-1,3-diene and 2,4-bis(1,3-cyclopentadienyl)-4-methyl-1-pentene. The latter compound is a new dimethylfulvene dimer whose monoanion had previously been proposed but not observed as an intermediate in the anionic oligomerization of dimethylfulvene.

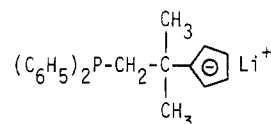
The addition of metal hydrides, Grignard reagents, and alkyllithiums to the C-6 position of fulvenes is a characteristic reaction of these systems and is, perhaps, the most efficient method for generating substituted cyclopentadienides for subsequent attachment to transition metals (eq 1).¹ The reaction proceeds in moderate to very



high yields for a variety of substituents R, R', and R'', failing only when steric hindrance to addition is extreme.² In the case of dimethylfulvene, the addition reactions of MH, RMgX, and RLi are invariably successful.

We report herein the details of the anomalous reactions of diphenylphosphinomethylolithium, (C₆H₅)₂PCH₂Li, with dimethylfulvene, reactions which were originally carried out in the hope that they would result in the efficient generation of the cyclopentadienide system **1**, possessing

remote tertiary phosphine functionality.³



Results

Reactions of (C₆H₅)₂PCH₂Li (2**) with Dimethylfulvene in Etheral Solvents.** By use of a procedure slightly modified from that described by Peterson and Hays,⁴ the alkyllithium **2** may be isolated as a white powder from the reaction of methyl diphenylphosphine and *n*-butyllithium in diethyl ether. This material is insoluble in petroleum ether and diethyl ether, but it readily dissolves in THF, giving yellow solutions. The NMR spectrum in THF displays a doublet (*J*_{PCH} = 3.5 Hz) due to the methylene protons at δ -0.34 ppm. Solid **2** is stable for months at room temperature when stored under dry N₂.

The reaction between (C₆H₅)₂PCH₂Li and dimethylfulvene in THF results almost immediately in a nearly colorless solution in which the upfield methylene doublet and the vinyl absorption of the starting materials are no longer visible, and the complex pattern due to the aromatic protons of **2** has been replaced by a narrowed multiplet at δ 7.28. A pair of apparent triplets are present at δ 5.64

(1) (a) Ziegler, K.; Shaefer, W. *Justus Liebigs Ann. Chem.* **1934**, 511, 101. (b) Knox, G. R.; Pauson, P. L. *Proc. Chem. Soc., London* **1958**, 289. (c) Knox, G. R.; Pauson, P. L. *J. Chem. Soc.* **1961**, 4610. (d) Knox, G. R.; Munro, J. D.; Pauson, P. L.; Smith, G. H.; Watts, W. E. *Ibid.* **1961**, 4619. (e) Renault, P.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1978**, 148, 35.

(2) Little, W. F.; Koestler, R. C. *J. Org. Chem.* **1961**, 26, 3245, 3247. Cram, D. J.; Wilson, D. R. *J. Am. Chem. Soc.* **1963**, 85, 1249.

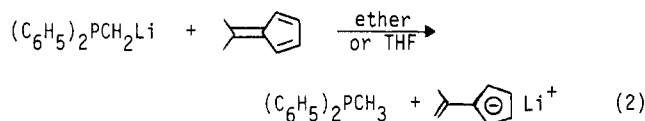
(3) A portion of this work was originally reported in preliminary form: Schore, N. E. *J. Am. Chem. Soc.* **1979**, 101, 7410.

(4) Peterson, D. J.; Hays, H. R. *J. Org. Chem.* **1965**, 30, 1939.

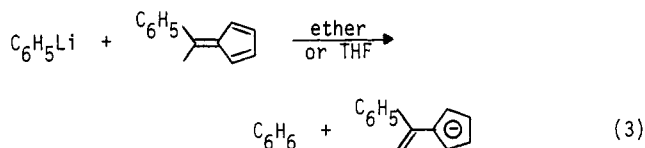
and 5.92. Although these observations are not inconsistent with the formation of the desired anion 1, this was quickly shown not to be the case. Removal of ca. 80% of the THF followed by treatment of the resultant solution with petroleum ether leads to precipitation of a solid whose NMR still possesses the vinylic absorptions at δ 5.64 and 5.92 but exhibits virtually no absorption in the aromatic region of the spectrum.

Very similar observations accompany the same reaction when carried out in diethyl ether. In this case the reaction is heterogeneous and requires several hours to go to completion (discharge of yellow color of fulvene). The white, THF-soluble solid present at the end of the reaction again displays vinyl but not phenyl absorption in the NMR.

These results were readily explained by repetition of the reaction in THF- d_6 . Addition of an equimolar amount of dimethylfulvene to a solution of 2 quantitatively generates a 1:1 mixture of methyldiphenylphosphine [δ 1.63 (d, J = 4 Hz) and 7.29 (m)] and a species which, in addition to the multiplets at δ 5.64 and 5.92 (each 2 H), displays signals at δ 2.08 (d, J = 1 Hz, 3 H), 4.28 (m, 1 H), and 4.89 (d, J = 3 Hz, 1 H), consistent with the conjugate base of dimethylfulvene, lithium isopropenylcyclopentadienide (eq 2). This assignment has been confirmed by generation



of the identical species via reaction of dimethylfulvene with lithium diisopropylamide. Lithium isopropenylcyclopentadienide has been identified as the product of the reactions of dimethylfulvene with both triphenylmethylsodium⁵ and sodamide in liquid NH_3 .¹² Deprotonation of dimethylfulvene by a reagent that could reasonably have been expected to undergo normal addition is unprecedented. A similar observation has, however, been made by Tainturier and co-workers in the reaction of phenyllithium with 6-methyl-6-phenylfulvene, which generates lithium (1-phenylethenyl)cyclopentadienide instead of the expected addition product (eq 3).⁶



Reaction of $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{Li}$ with Dimethylfulvene in Petroleum Ether. Addition reactions of organolithium reagents may be favored over proton abstraction by reduction of the polarity of the reaction medium.⁷ We therefore chose to investigate what sort of reaction, if any, would take place in the heterogeneous mixture of 2 and dimethylfulvene in the presence of hydrocarbon solvent. A petroleum ether solution 0.1 M in dimethylfulvene treated with an equimolar quantity of solid 2 at 27 °C only very slowly loses the color of the fulvene. After 7 days, however, the fulvene is completely consumed, leaving a white solid suspended in a solution from which essentially pure methyldiphenylphosphine may be isolated in ca. 80% yield. In spite of the apparent predominance of the pro-

Table I. Major NMR Signals at 360 MHz due to a Mixture of Ether-Insoluble and Petroleum Ether Insoluble Species Formed from Reaction of 2 and Dimethylfulvene in Petroleum Ether

chemical shift, δ	appearance	approx integr
2.21	d, J = 12.5 Hz	1 H
2.57	s	2 H
2.90	d, J = 12.5 Hz	1 H
4.42	d, J = 3.8 Hz	1 H
4.81	d, J = 3.8 Hz	1 H
5.27	"t", splitting = 2.7 Hz	2 H
5.40	"t", splitting = 2.7 Hz	2 H
5.43	"t", splitting = 2.6 Hz	2 H
5.50	"t", splitting = 2.6 Hz	2 H
5.57	"t", splitting = 2.5 Hz	2 H
5.74	"t", splitting = 2.5 Hz	2 H

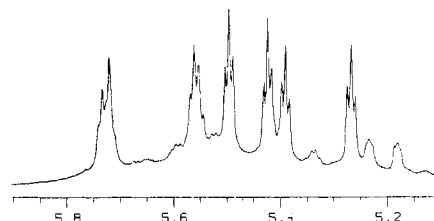
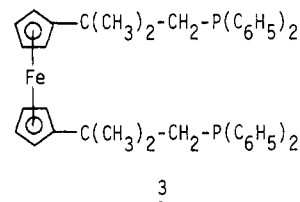


Figure 1. Cyclopentadienyl region of the 360-MHz NMR for the mixture of lithium cyclopentadienide species obtained from reaction of 2 with dimethylfulvene in petroleum ether, after removal of ether-soluble components. Decoupling experiments indicate the following pairs of multiplets are mutually coupled (in δ): 5.27 and 5.43, 5.40 and 5.50, 5.57 and 5.74. The signal at δ 5.70 is due to an impurity of 1. Multiplets at δ 5.19, 5.33, and 5.60 were subsequently identified with protons on the disubstituted cyclopentadienyl ring of 5.

ton-transfer process, analysis of the solid product shows little or no lithium isopropenylcyclopentadienide by NMR. Instead, a mixture of several new organolithium species is indicated by the complexity of the absorptions both in the olefinic and aliphatic regions of the spectrum.

Partial separation of the mixture is achieved by exhaustive extraction of the solid with diethyl ether. The soluble portion is found to consist almost entirely of the phosphine-containing cyclopentadienide 1, the original synthetic goal of these experiments, in 12% yield. This material has been characterized in solution by NMR and by conversion in good yield to the corresponding ferrocene 3 by reaction with anhydrous ferrous chloride in ether.



The mixture of ether-insoluble and petroleum ether insoluble organolithium species remaining after the removal of 1 was then subjected to 360-MHz NMR analysis. Significant signals, aside from the complex array of methyl absorptions upfield of δ 2, are listed in Table I. This material also exhibits phenyl absorptions corresponding in integrated intensity to ca. 7% of the original [(diphenylphosphino)methyl]lithium. The most informative portions of the spectrum include a pair of coupled doublets (J = 12.5 Hz) at δ 2.21 and 2.90, possibly due to two nonequivalent protons of a methylene group in a ring, a second pair of coupled doublets (J = 3.8 Hz) at δ 4.42 and 4.81, most likely resulting from a terminal vinyl group, and the region between δ 5 and 6, which is illustrated in Figure

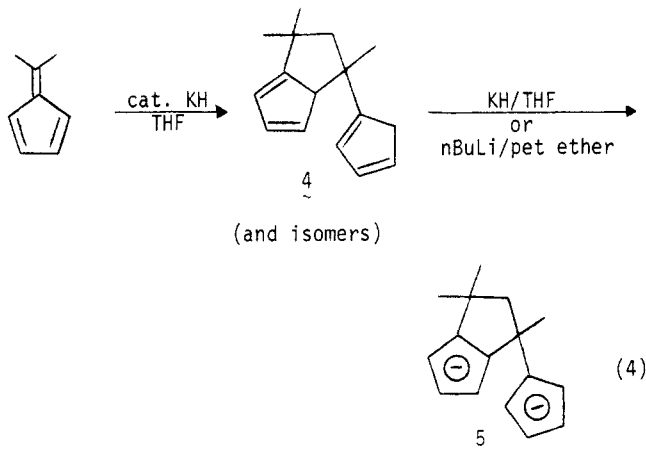
(5) Schlenck, W.; Bergmann, E. *Justus Liebigs Ann. Chem.* 1930, 479, 58.

(6) Couturier, S.; Gautheron, B.; Renaut, P.; Tainturier, G. *C. R. Hebd. Seances Acad. Sci., Ser. C* 1977, 284, 323.

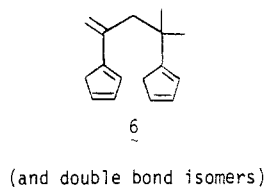
(7) Schlosser, M. "Struktur und Reaktivität polarer Organometalle"; Springer-Verlag: New York, 1973; p 148 and references therein.

1. Six multiplets, all apparent triplets, are clearly evident, along with several absorptions of lesser intensity. Decoupling experiments indicate that these triplets are coupled in a pairwise fashion (Figure 1), consistent with each being half of an AA'XX' pattern characteristic of a monosubstituted cyclopentadienide system and there being a total of three different rings of this type in the major component(s) of the product mixture. The 360-MHz NMR also reveals the presence of lithium isopropenylcyclopentadienide, in extremely small quantity.

Quenching of this organolithium product mixture with aqueous KH_2PO_4 gives rise to a yellow oil with an odor reminiscent of dimethylfulvene. Analysis of this oil by GC/MS reveals the presence of a number of oligomers of dimethylfulvene. By far the major components are dimeric (m/e 212) although significant quantities of trimers are present along with traces of higher molecular weight volatile materials and two monomeric species. Conventional preparative GC allowed the separation and collection of two dimeric fractions. The fraction with the earlier retention time is the major dimeric product, comprising approximately half of the entire mixture. This compound is identical with the major product isolated from the anionic polymerization of dimethylfulvene, 6-(1,3-cyclopentadienyl)-6,8,8-trimethylbicyclo[3.3.0]octa-1,3-diene (4), and its double bond isomers.⁸ Deprotonation of 4 with either KH in THF or *n*-BuLi in petroleum ether gives rise to the dianion 5 (eq 4), whose NMR spectrum is superimposable⁹ with a portion of the NMR spectrum of the 2-dimethylfulvene product mixture (signals at δ 2.21, 2.90, 5.57, and 5.74 in Table I).



The second major dimeric component of the quenched mixture appears to possess structural type 6, one that has



not heretofore been isolated from dimethylfulvene reaction mixtures. Like 4, 6 has a very complex NMR spectrum at 360 MHz. Unlike 4, however, 6 displays several pairs of signals in the region δ 4.5–5.3, characteristic of the terminal vinyl protons of the various double bond iso-

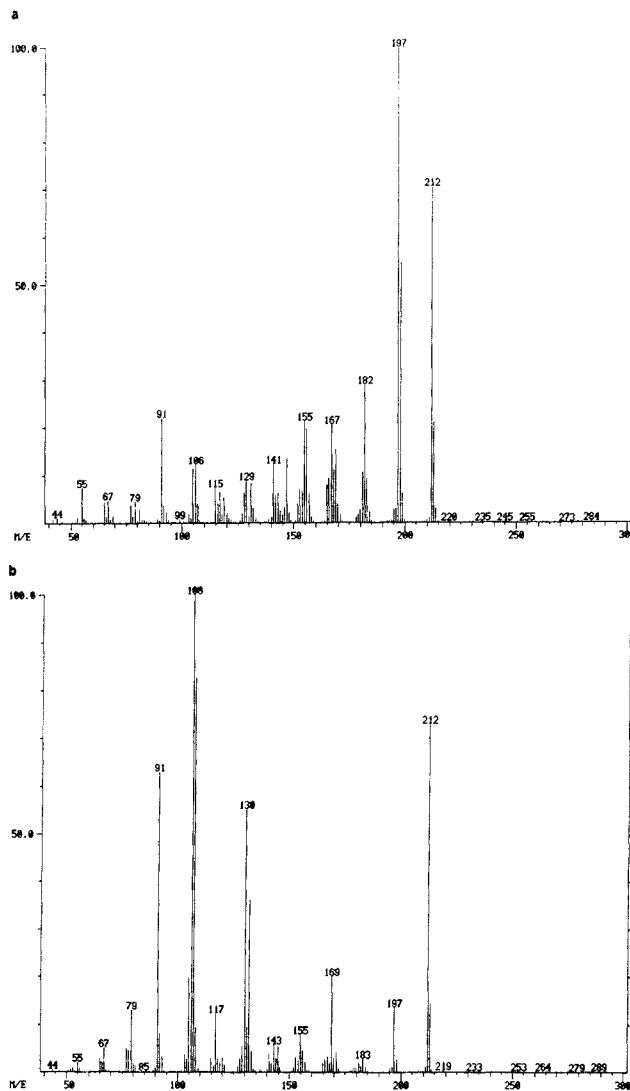


Figure 2. (a) GC/MS trace identified with one double bond isomer of 4. (b) GC/MS trace identified with one double bond isomer of 6.

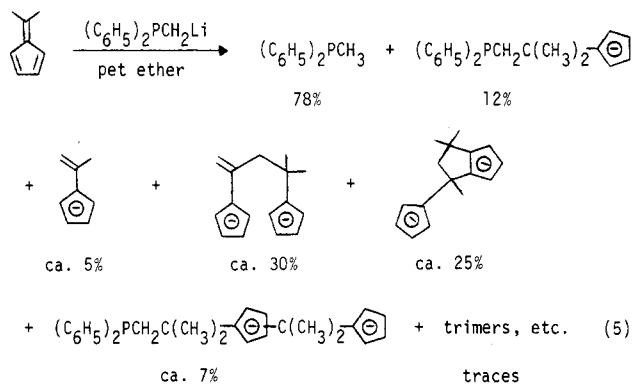
mers.¹⁰ Dimer 6 appears to be rather unstable, exhibiting significant changes in its NMR spectrum upon attempted GC collection. The compound is not stable to extended storage at 0 °C. Therefore, characterization rests chiefly upon NMR data from freshly prepared mixtures with 4, GC/MS data, and characterization of the dilithium salt 7. The latter is readily identified by NMR (Table I, signals at δ 2.57, 4.42, 4.81, 5.27, 5.40, 5.43, and 5.50). Significantly, the isomers of compound 6, in accord with their relatively simple structure, undergo mass spectrometric fragmentation to yield predominantly monomer-derived ions, e.g., m/e 106 and 107. Dimer 4, in contrast, fragments predominantly via loss of a methyl group and shows very little fragmentation to monomer, a process that requires the breaking of two carbon–carbon bonds (Figure 2).

None of the higher molecular weight species formed in these reactions was present in sufficient quantity for full structural elucidation. On the basis of GC/MS evidence, however, these species are likely to be derived simply by the addition of anion 1, dianion 5, and dianion 7 to another molecule of dimethylfulvene. The overall reaction between 2 and dimethylfulvene in petroleum ether is described by eq 5.

(8) Slongo, M.; Kronig, P.; Neuenschwander, M. *Makromol. Chem.* 1979, 180, 259.

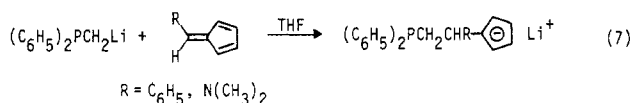
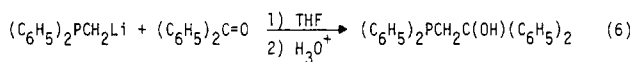
(9) The dilithium salt spectrum is superimposable while the dipotassium salt exhibits small (≤ 0.2 ppm) shifts in the positions of several of its absorptions.

(10) Compare spectra of the double bond isomers of dimethylfulvene itself: Hine, J.; Knight, D. B. *J. Org. Chem.* 1970, 35, 3946.



Discussion

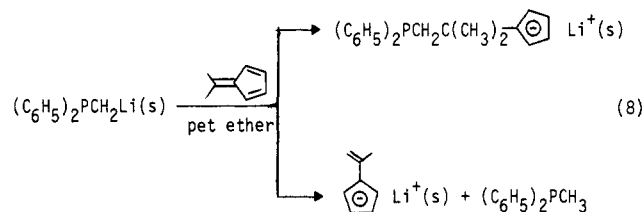
At first glance, the tendency of [(diphenylphosphino)methyl]lithium (**2**) in ether or THF to deprotonate dimethylfulvene is surprising. Explanations based upon steric effects are inadequate. Additions of carbanionic species to substituted fulvenes to give product considerably more hindered than **1** are well-known and facile reactions.¹ Furthermore, **2** is itself quite capable of addition reactions to hindered substrates such as benzophenone,^{4,11} as well as to both 6-phenylfulvene and 6-(dimethylamino)fulvene³ (eq 6 and 7). The anomalous behavior of **2** toward di-



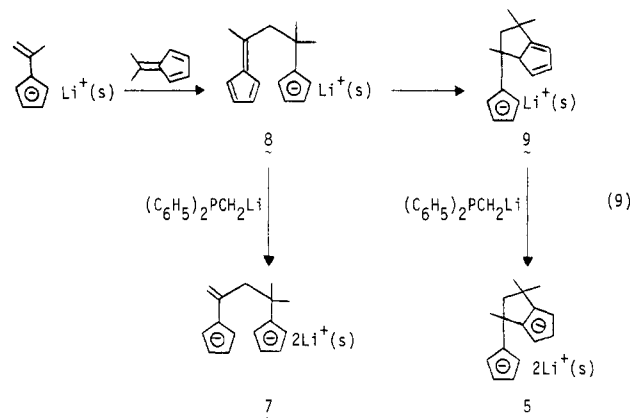
methylfulvene must at least in part be due to an unusually enhanced kinetic basicity of the reagent, rather than some peculiar inability to behave as a normal nucleophile. This enhanced basicity may reasonably be ascribed to an increase in the carbanionic character of **2** relative to simple alkyl lithium reagents, perhaps as a result of coordination of the lithium counterion with the phosphine lone pair.¹² In reactions of alkyl lithium reagents with enolizable ketones, the use of hexamethylphosphoric triamide (HMPA) as solvent is known to divert the predominant reaction pathway from addition to enolization.⁷ HMPA is obviously functionally very different from a tertiary phosphine, however, and we are unaware of any comparable effects resulting from the presence of the latter type of compound in a reaction of this type. In particular, we have been unsuccessful in attempts to divert the *n*-butyllithium reaction with dimethylfulvene from addition to deprotonation by carrying out the reaction in the presence of tertiary phosphine. It is likely, therefore, that the behavior of **2** results from the combined effects of moderate steric hindrance to addition and increased basicity due to the presence of the phosphine moiety, where neither effect alone would have been sufficient to bring about the observed changes in reactivity. This conclusion must be considered tentative, however, due to the relatively small amount of information currently available concerning this particular anionic system.

The reaction between **2** and dimethylfulvene in petroleum ether introduces the additional feature of near total

insolubility of one of the starting materials and virtually all the intermediate products. The primary reactions must occur on the surface of suspended **2**, yielding products that, themselves, are insoluble (eq 8). Further reaction of



lithium isopropenylcyclopentadienide with dimethylfulvene must be rapid relative to its initial formation to account for the preponderance of oligomers even when the original starting materials are present in equimolar quantities. This reaction leads to the major dimeric products via the same pathway as described by Slongo et al.⁸ for the homogeneous anionic polymerization of dimethylfulvene (eq 9). The one difference in the hetero-



geneous system is the successful trapping out of the proposed intermediate **8** by deprotonation, in competition with its intramolecular cyclization to **9**. Given the fact that the initial deprotonation of dimethylfulvene by **2** is slow in petroleum ether, it is logical to assume that the deprotonation of **8** is also a slow process, and, by inference, so is its intramolecular cyclization. Since the cyclization of **8** is in fact quite rapid in homogeneous media (THF),⁸ it would appear that the sluggishness of this process in our system is derived from solid-state effects such as the predominance of a conformation unfavorable for cyclization or the presence of sterically hindering ion aggregates.

In summary, [(diphenylphosphino)methyl]lithium demonstrates an unusual preference toward deprotonation of dimethylfulvene both in homogeneous and heterogeneous media. Only in hydrocarbon solvent is the product of the expected addition process obtained, and that in only very minor amounts. The major products obtained are those expected from the heterogeneous reaction of dimethylfulvene with the lithium salt of its conjugate base. Studies aimed at uncovering similar sorts of anomalous reactivity from related phosphine-derived anions are currently underway.

Experimental Section

General Methods. Dimethylfulvene was prepared by a literature procedure,¹³ distilled, degassed, and stored under N₂ at -40 °C. Dimethylfulvene dimer **4** was prepared according to a modified literature procedure⁸ by using KH as the polymerization

(11) Peterson, D. J. *J. Organomet. Chem.* **1967**, *8*, 199.

(12) Although the pK_a of methyl diphenyl phosphine has not been reported, it is not deprotonated by lithium diisopropylamide, and even its reaction with *n*-butyllithium is exceedingly slow.

(13) Crane, G.; Boord, C. E.; Henne, A. L. *J. Am. Chem. Soc.* **1945**, *67*, 1237.

catalyst instead of C_5H_5Na . The product was distilled under high vacuum (bath temperature $\leq 150^\circ C$) and stored under N_2 at $-40^\circ C$. Methylidiphenylphosphine, *n*-butyllithium in hexane, and all the NMR solvents were obtained commercially and stored under N_2 . Reaction solvents were distilled from sodium-benzophenone, admixed with tetraglyme when necessary, and stored over Na under N_2 . All reactions were carried out under an atmosphere of purified N_2 . NMR spectra were recorded on Varian A-60A and EM-390 and Nicolet NT-360 instruments. Microanalyses were carried out at the University of California at Berkeley microanalytical laboratory. GC/MS experiments were carried out at the University of California at Davis Facility for Advanced Instrumentation.

[(Diphenylphosphino)methyl]lithium⁴ (2). A solution of methylidiphenylphosphine (15.0 g, 0.075 mol) in 100 mL ether was treated with 40 mL of 2.2 M *n*-butyllithium in hexane (0.088 mol) and the yellow mixture allowed to stir under N_2 at $27^\circ C$ for 3 days. The reaction mixture was then diluted with 100 mL of petroleum ether and the product collected by filtration under N_2 ; yield 5.5 g (35%); white solid; NMR (THF) δ -0.34 (d, J = 3.5 Hz, 2 H), 6.8–7.1 (m, 6 H), 7.2–7.6 (m, 4 H). The compound undergoes very slight discoloration upon extended storage under N_2 at $27^\circ C$. This does not appear to affect its reactivity in any significant way.

Reaction of 2 with Dimethylfulvene in Ether. A solution of 0.042 g (0.40 mmol) of dimethylfulvene in 1.5 mL of ether was treated with 0.085 g (0.41 mmol) of solid 2 in portions over a period of 5 min under N_2 , and the heterogeneous mixture was stirred for 18 h. Upon dilution of the mixture with 15 mL of petroleum ether, 0.039 g of lithium isopropenylcyclopentadienide (87% yield) was isolated as a white solid. A NMR (THF) spectrum identical with that observed in the following experiment was observed.

Reaction of 2 with Dimethylfulvene in THF- d_6 . A solution containing 0.021 g (0.20 mmol) of dimethylfulvene and 0.042 g (0.21 mmol) of 2 in 0.5 mL of THF- d_6 was prepared and examined by NMR. Quantitative conversion to methylidiphenylphosphine [δ 1.63 (d, J = 4 Hz, 3 H), 7.2–7.6 (m, 10 H)] and lithium isopropenylcyclopentadienide [δ 2.10 (d, J = 1 Hz, 3 H), 4.30 (qd, J = 1, 3 Hz, 1 H), 4.90 (d, J = 3 Hz, 1 H), 5.67 (apparent t, splitting = 2.5 Hz, 2 H), 5.95 (apparent t, splitting = 2.5 Hz, 2 H)] was observed. The latter spectrum was superimposable with that obtained from the reaction of 0.070 g (0.66 mmol) of dimethylfulvene with 0.070 g (0.66 mmol) of lithium diisopropylamide in THF.

Reaction of 2 with Dimethylfulvene in Petroleum Ether. A solution of 0.50 g (4.72 mmol) of dimethylfulvene in 50 mL of petroleum ether was treated with 1.00 g (4.85 mmol) of solid 2, and the heterogeneous mixture was stirred for 7 days. The white solid present was collected and thoroughly washed with petroleum ether (3×25 mL). Evaporation of the latter afforded 0.75 g (78% yield) of pure methylidiphenylphosphine.

The petroleum ether insoluble solids were next thoroughly washed with ether (3×35 mL). The combined ether extracts were evaporated, yielding 0.18 g (12%) of a brownish oil, identified as slightly impure lithium [1,1-dimethyl-2-(diphenylphosphino)ethyl]cyclopentadienide (1): NMR (THF- d_6) δ 1.23 (s, 6 H), 2.60 (d, J = 5 Hz, 2 H), 5.70 (br s, 4 H), 7.2–7.7 (m, 10 H). This material was further characterized by conversion to the ferrocene derivative (below).

The ether-insoluble solid remaining after the removal of 1 weighed 0.57 g, accounting for an additional 7% of the original 2 and 90% of the dimethylfulvene by NMR. The mass balance overall is therefore virtually quantitative with respect to both starting materials. This solid was found to contain two major components by NMR at 360 MHz: dilithium salts 5 and 7. Although these materials could not be separated, the independent synthesis of one of them (5; see below) allowed the unambiguous assignment of all major peaks in the NMR spectrum of the mixture in terms of these two components. For 5: NMR (THF- d_6 , 360 MHz) δ 1.25 (s, 3 H), 1.33 (s, 3 H), 1.58 (s, 3 H), 2.21 (d, J = 12.5 Hz, 1 H), 2.90 (d, J = 12.5 Hz, 1 H), 5.19 (dd, J = 1.5, 3 Hz, 1 H), 5.33 (dd, J = 1.5, 3 Hz, 1 H), 5.57 (apparent t, splitting = 2.5 Hz, 2 H), 5.60 (dd, J = 3, 3 Hz, 1 H), 5.74 (br s, 2 H). For

7: NMR (THF- d_6) δ 1.33 (s, 6 H), 2.57 (s, 2 H), 4.42 (d, J = 3.8 Hz, 1 H), 4.81 (d, J = 3.8 Hz, 1 H), 5.27 (apparent t, splitting = 2.7 Hz, 2 H), 5.40 (apparent t, splitting = 2.7 Hz, 2 H), 5.43 (apparent t, splitting = 2.6 Hz, 2 H), 5.50 (apparent t, splitting = 2.6 Hz, 2 H). Extensive decoupling experiments confirmed all the interactions expected on the basis of the structures proposed for 5 and 7, both in the above reaction mixture and (for 5) in the independently synthesized material. Anal. Calcd for $(C_9H_9Li)_n$: C, 85.71; H, 8.04; Li, 6.20. Found: C, 82.18; H, 8.44; Li, 4.58.

A sample of this solid mixture was protonated by treatment with 0.5 M aqueous KH_2PO_4 . The organic materials were extracted into ether, and the solution was dried (Na_2SO_4) and stripped. NMR analysis revealed the presence of the known⁸ dimethylfulvene dimer 4, corresponding to protonated 5, as well as the presence of a material with major absorptions at δ 1.15 (s), 1.20 (s), 1.40 (br s), 2.5–3.1 (m), 4.80 (m), 5.20 (m), 5.28 (m), and 5.8–6.6 (m), presumed to be a mixture of double-bond isomers of 6, i.e., protonated 7. GC/MS analysis confirmed that the major components in the mixture were dimers whose mass spectra fell into two categories: those having intense peaks corresponding to fragmentation to monomers (structure 6) and those lacking such peaks (structure 4). Dimer 4 was successfully isolated via GC collection (10 ft \times $1/4$ in. column, 3% SE-30 on Chromasorb W, glass, $150^\circ C$) and shown to be identical with an independently prepared sample. A second major component with a retention time expected for a dimer was also collected. Although its NMR showed vinyl signals in the δ 4.5–5.2 region, the spectrum as a whole was very different from (and much more complicated than) that exhibited by 6 in the crude mixture before GC.

1,1'-Bis[1,1-dimethyl-2-(diphenylphosphino)ethyl]ferrocene (3). A solution of 0.18 g (0.58 mmol) of 1 was dissolved in 2 mL of ether and added to a stirred mixture of excess anhydrous $FeCl_2$ in 2 mL of ether. After 24 h of being stirred under N_2 , the brown solution was filtered, stripped to a brown oil, and chromatographed (1:1 benzene-petroleum ether, alumina of activity I). Ferrocene 3 was isolated as a yellow-orange solid weighing 0.13 g (66% yield) after being washed with cold ($-40^\circ C$) petroleum ether: mp 136–137 (benzene-petroleum ether, $-40^\circ C$); NMR (C_6D_6) δ 1.58 (s, 12 H), 2.57 (d, J = 3 Hz, 4 H), 4.13 (br s, 8 H), 7.2–7.9 (m, 20 H). Anal. Calcd for $C_{22}H_{44}P_2Fe$: C, 75.67; H, 6.65. Found: C, 75.83; H, 6.78.

Dilithium and Dipotassium Salts of 4 (5) (NMR Experiments). A solution of 4 in petroleum ether was treated with a slight excess of *n*-butyllithium in hexane. After several hours a white precipitate had formed which was collected and analyzed by NMR (see above).

The corresponding dipotassium salt was prepared by treatment of a THF- d_6 solution of 4 with excess solid KH: NMR (THF- d_6 , 360 MHz) δ 1.27 (s, 3 H), 1.33 (s, 3 H), 1.73 (s, 3 H), 2.13 (d, J = 12.7 Hz, 1 H), 2.97 (d, J = 12.7 Hz, 1 H), 4.97 (dd, J = 1.5, 3.0 Hz, 1 H), 5.15 (dd, J = 1.5, 3.0 Hz, 1 H), 5.40 (apparent t, splitting = 3.0 Hz, 2 H), 5.48 (dd, J = 3.0, 3.0 Hz, 1 H), 5.63 (apparent t, splitting = 3.0 Hz, 2 H). A very small amount of potassium isopropenylcyclopentadienide was also observed in the solution: NMR (THF- d_6 , 360 MHz) δ 1.94 (br s, 3 H), 4.02 (br s, 1 H), 4.64 (d, J = 3.0 Hz, 1 H), 5.59 (m, 2 H), 5.81 (m, 2 H).

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