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The First Noncoordinated Phosphonium Diylide, $[Me_2P(C_{13}H_8)_2]^-$, and Its Ylidic and Cationic Counterparts: Synthesis, Structural Characterization, and Interaction with the Heavy Group 2 Metals

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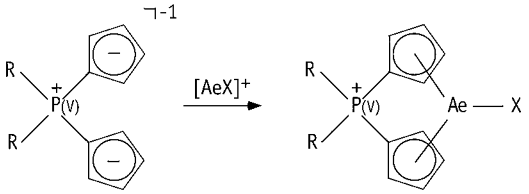
Treatment of potassium or lithium fluorenide with $MePCl_2$ generates the organophosphine $MeP(C_{13}H_9)_2$, which on reaction with methyl iodide produces the phosphonium species $[Me_2P(C_{13}H_9)_2]I$ in 74% yield. In the solid state, H···I contacts of <3.3 Å help generate a layered structure in which the fluorenyl rings are nearly parallel. On subsequent reaction of $[Me_2P(C_{13}H_9)_2]I$ with either KH or $K[N(SiMe_3)_2]$, the corresponding neutral phosphoylide, $Me_2P(C_{13}H_9)(C_{13}H_8)$, forms in 67% yield and was structurally characterized. The phosphonium iodide $[Me_2P(C_{13}H_9)_2]I$ was allowed to react with $Ae[N(SiMe_3)_2]_2$ (Ae = Ca, Ba), and the product from the reaction with the calcium complex was structurally identified as the salt $[CaI(thf)_5][Me_2P(C_{13}H_8)_2]$. The anion, which is outside the coordination sphere of the calcium, represents the first structurally authenticated example of a free phosphonium diylide. The P−C(ylidic) bond length of 1.748(4) Å reflects some partial multiple bond character. ^1H and ^{31}P NMR spectra suggest that the barium analogue is similar. Density functional theory calculations were performed on representative phosphonium diylides as an aid to interpreting the bonding in this class of compounds. Despite the strong electrostatic attraction that usually drives metal−ligand binding in highly ionic systems, calcium and barium prefer to coordinate to a single iodide ion and several neutral oxygen donors rather than to the charged diylide.

Introduction

Organometallic compounds of the heavy group 2 elements (Ca−Ba) depend on the presence of bulky ligands to provide steric support for the metals' large coordination environments.[1] Multiply substituted cyclopentadienyl rings such as $[C_5(i\text{-}Pr)_4H]^-$,[2,3] $[C_5(i\text{-}Pr)_5]^-$,[4] and $[C_5(SiMe_3)_3H_2]^-$ [5] have proven to be valuable for this chemistry, but excessive congestion at the metal center can interfere with subsequent reactions.[6] The development of ligands with steric profiles different from those of individual $[C_5R_nH_{5-n}]^-$ rings is a highly desirable goal.

Bridged $R_nECp'_2$ species represent such an alternative class of ligands, and many dialkyl- and diarylsilyl examples are known because of their use in group 4 based polymerization catalysts.[7−10] In principle, *phosphorus*-bridged cyclopentadienyl ligands could exhibit an even wider range of structural types than their silyl-based analogues, as a phosphorus bridge can contain either P(III) or P(V). The former oxidation state is represented by the phosphine ligands $[RP(Cp')_2]^{-2}$,[11] whereas pentavalent phosphorus is found in the phosphine oxide based anions $[R(O)P(Cp')_2]^{-2}$ [12,13] and the diylides $[R_2P(Cp')_2]^-$.[14] The latter are potentially attractive ligands for the group 2 elements, as they could simultaneously provide a bulky metallocene-like framework, yet still allow the metal to bind an additional anionic ligand in an electrically neutral complex (Scheme 1).

Scheme 1. An *ansa*-Phosphonium Bridging Ligand Illustrating the "Metallocene-like" Skeleton with Its Monoanionic Charge, and the Possible Complex between an $[AeX]^+$ Fragment and $[R_2P(Cp')_2]^-$



Despite their presumably strong nucleophilicity and the possibility of serving as multifunctional ligands,[15] phosphonium diylides have not been widely employed in coordination

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chemistry.[14] $[R_2P(CHR')_2]^-$ anions are most commonly encountered as their alkali metal salts, although complexes with some transition metals (e.g., Cr^{3+}, Ag^+, Ni^{2+}, Cu^{2+}) are also known.[16−18] Group 2 examples are limited to a barium complex of a pyridine-substituted phosphonium bis(methylide),[19] the barium phosphonium dibenzylide species $[Ph_2P(4\text{-methylbenzylide})_2]_2Ba$,[20] and several barium derivatives of the phosphonium dicyclopentadienylide $[R_2P(2\text{-Me-4-}t\text{-BuC}_5H_2)_2]^-$ (R = Me, *n*-Bu).[21]

We were interested in incorporating the fluorenyl anion (Fl^-) into a phosphonium-bridged ligand to use with the alkaline-earth metals. Formally related to the cyclopentadienyl ring,[22] the fluorenide anion displays a variety of coordination modes with metal ions, and a silicon-bridged bis(fluorenylide) complex has been prepared with calcium and barium.[23] The metal centers in $[Me_2Si(Fl)_2](Ca,Ba)(thf)_n$ exhibit distorted (η^3, η^3) and (η^3, η^5) binding to the fluorenyl rings, but a phosphonium-bridged version, with its shorter P−C bonds, might encourage a more symmetrical and kinetically stable (η^5, η^5) ligation. As described below, this proves not to be the case; the $[Me_2P(Fl)_2]^-$ anion displays little nucleophilicity toward group 2 cations and is actually the first uncomplexed phosphonium diylide to be structurally authenticated.

Experimental Section

General Considerations. Unless otherwise specified, all manipulations were performed with the rigorous exclusion of air and moisture using high-vacuum, Schlenk, or glovebox techniques. Proton, carbon ($^{13}C\{^1H\}$), and phosphorus ($^{31}P\{^1H\}$) NMR spectra were obtained at 20 °C on a Bruker DPX-300 at 300, 75.5, and 121.4 MHz, respectively, and were referenced to the residual proton and ^{13}C resonances of C_6D_6 (δ 7.15 and 128.0), THF-d_8 (δ 3.58 and 67.4), or DMSO-d_6 (δ 2.50 and 39.5) or, for ^{31}P NMR, an external standard of H_3PO_4. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Infrared data were obtained on an ATI Mattson-Genesis FT-IR spectrometer either as KBr pellets as previously described[2] or as neat samples sealed between KBr plates. Melting points were determined in sealed capillaries for air- or moisture-sensitive compounds.

Materials. Anhydrous calcium, strontium, and barium iodide were commercial samples (Strem or Cerac, 95%) and were heated under vacuum (150 °C, 10^{-4} Torr) to ensure complete removal of water and residual amounts of free iodine. Potassium hydride was purchased from Strem and washed with hexanes in a glovebox prior to use. Fluorene, $HN(SiMe_3)_2$, $MePCl_2$, methyl iodide, and CD_2Cl_2 were purchased from Strem, Acros, or Aldrich and used as received. Butyllithium was purchased from Aldrich as a 2.5 M solution in hexanes. Diethyl ether, THF, toluene, and hexanes were distilled under nitrogen from potassium benzophenone ketyl.[24] Methylene chloride was distilled under nitrogen from CaH_2. C_6D_6 and THF-d_8 were vacuum distilled from Na/K (22/78) alloy; DMSO-d_6 was distilled from CaH_2. All solvents for NMR were stored over 4A molecular sieves prior to use.

Synthesis of Calcium Bis(hexamethyldisilazide), $Ca[N(SiMe_3)_2]_2$. Potassium hydride (0.615 g, 15.3 mmol) was added to a solution of $HN(SiMe_3)_2$ (2.476 g, 15.3 mmol) in toluene (70 mL), and the resulting slurry was stirred until no further gas evolution occurred (ca. 3 h). The turbid solution was filtered over a medium-porosity frit into a separate flask. Calcium iodide (2.25 g, 7.66 mmol) was added to the filtrate, and the resulting mixture was stirred for 48 h. The solution was filtered to remove insoluble material, and the toluene filtrate was stripped to dryness. Hexanes (2 × 15 mL) were added and removed under vacuum to assist in removal of volatile impurities. Removal of the hexanes and prolonged drying under vacuum afforded 2.21 g (80%) of $Ca[N(SiMe_3)_2]_2$ as a fluffy white powder, which was characterized by comparison of its ^1H NMR shifts in C_6D_6 (δ 0.30 and 0.24) with literature values.[25]

Synthesis of Strontium Bis(hexamethyldisilazide), $Sr[N(SiMe_3)_2]_2$. In a procedure similar to that used for the calcium compound, $K[N(SiMe_3)_2]$ (3.06 g, 15.3 mmol) was prepared in toluene and the reaction mixture filtered to yield a clear solution. Strontium iodide (2.61 g, 7.65 mmol) was added to the filtrate, and the resulting mixture was treated as for the calcium compound, leaving 2.87 g (92%) of $Sr[N(SiMe_3)_2]_2$ as a fluffy off-white powder, which was characterized by comparison of its ^1H NMR shifts in C_6D_6 (δ 0.22 and 0.13) with literature values.[25]

Synthesis of Barium Bis(hexamethyldisilazide), $Ba[N(SiMe_3)_2]_2$. In a procedure similar to that used for the calcium compound, $K[N(SiMe_3)_2]$ (3.06 g, 15.3 mmol) was prepared in toluene and the reaction mixture filtered to yield a clear solution. Barium iodide (3.00 g, 7.67 mmol) was added, and the resulting mixture was treated as for the calcium compound, leaving 2.69 g (77%) of $Ba[N(SiMe_3)_2]_2$ as a fluffy tan powder, which was characterized by comparison of its ^1H NMR shift in C_6D_6 (δ 0.24) with literature values.[25,26]

Synthesis of Methylbis(fluorenyl)phosphine, $MeP(FlH)_2$. Fluorene (11.20 g, 67.4 mmol) was dissolved in 300 mL of a 1:1 mixture of Et_2O and hexanes in a 500 mL Schlenk flask. At 0 °C, 26.9 mL of a 2.5 M hexanes solution of *n*-BuLi (67.3 mmol) was added dropwise. The solution immediately began turning orange, and a precipitate soon formed. After 3 h, the solution was allowed to warm to room temperature. The mixture was then cooled to −40 °C, and $MePCl_2$ (3.0 mL, 34 mmol) was slowly added. The low temperature was maintained for approximately 1 h, after which the mixture was allowed to warm to room temperature. The slurry was stirred at room temperature for an additional 3 h. The solvent was then removed under vacuum to afford a dark orange oil. Freshly distilled CH_2Cl_2 was added, which yielded a dark orange solution and a white solid (LiCl). The mixture was filtered using a medium-porosity Schlenk frit, followed by removal of the CH_2Cl_2 from the filtrate under vacuum to leave an orange solid. The solid was washed with hexanes (3 × 25 mL) to afford off-white $MeP(FlH)_2$ (10.50 g, 83%). ^1H NMR (DMSO-d_6): δ 8.01−7.99 (multiplet, 8H, ring Fl); 7.66−7.33 (multiplet, 8H, ring Fl); 4.66 (singlet (br), 2H, $CH_3PC\mathit{H}(Fl)$); 0.47 (doublet, J = 5.8 Hz, 3H, $C\mathit{H}_3PCH(Fl)$). ^{31}P NMR (DMSO-d_6): δ −2.18.

Synthesis of Methylbis(fluorenyl)phosphine Oxide, $Me(O)P(FlH)_2$. $MeP(FlH)_2$ (0.25 g, 0.66 mmol) was exposed to the air in the solid state for 48 h. The initially off-white solid became uniformly tan in color, and $Me(O)P(FlH)_2$ was isolated in quantitative yield, mp 216−218 °C. Anal. Calcd for $C_{28}H_{24}OP$: C, 82.52; H, 5.94; P, 7.60. Found: C, 83.30; H, 5.48; P, 7.83. ^1H NMR (CD_2Cl_2): δ 7.81 (doublet, 4H, ring Fl); 7.58 (doublet, 2H, ring Fl); 7.43 (doublet, 2H, ring Fl); 7.32−7.30 (multiplet, 4H, ring Fl); 7.24−7.22 (multiplet, 4H, ring Fl); 4.58 (singlet (br), 2H, $CH_3PC\mathit{H}(Fl)$); 0.47 (doublet, J = 2.1 Hz, 3H, $C\mathit{H}_3PCH(Fl)$). ^{31}P NMR (CD_2Cl_2): δ −1.1. ^{13}C NMR (CD_2Cl_2, 20 °C): δ 144.6 ($CH_3P\mathit{C}H(Fl)$); 142.0 ($\mathit{C}H_3PCH(Fl)$); 127.7 (ring Fl); 127.6 (ring Fl); 127.5 (ring Fl); 126.1 (ring Fl); 125.8 (ring Fl); 121.1 (ring Fl); 120.9 (ring Fl).

Synthesis of Dimethylbis(fluorenyl)phosphonium Iodide, $[Me_2P(FlH)_2]I$ (I). $MeP(FlH)_2$ (7.71 g, 20.5 mmol) was added to a flask equipped with a magnetic stirring bar and 300 mL of THF. Methyl

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iodide (2.91 g, 20.5 mmol) was added, and the mixture was stirred. A fine white precipitate began to form after 1 h, and the stirring was continued overnight. The slurry was then filtered over a medium-porosity frit, and the solid was washed with hexanes to afford 7.80 g (73%) of $[Me_2P(FlH)_2]I$ (**I**), mp 316 °C. Anal. Calcd for $C_{28}H_{24}IP$: C, 64.88; H, 4.68; P, 5.97. Found: C, 64.50; H, 4.45; P, 6.27. ^1H NMR (DMSO-d_6): δ 7.80 (doublet, $J = 7.6$ Hz, 4H, ring Fl); 7.54 (doublet, $J = 7.7$ Hz, 4H, ring Fl); 7.44 (triplet, $J = 7.6$ Hz, 4H, ring Fl); 7.21 (triplet, $J = 7.5$ Hz, 4H, ring Fl); 5.46 (doublet, $J = 18.1$ Hz, 2H, CH_3PCH); 2.03 (doublet, $J = 13.2$ Hz, 6H, PCH_3). ^{31}P NMR (DMSO-d_6): δ 36.0. ^{13}C NMR (DMSO-d_6): δ 141.3 (doublet, $CH_3PCH(Fl)$); 135.5 (doublet, $CH_3PCH(Fl)$); 129.0 (singlet, Fl); 128.6 (singlet, Fl); 127.5 (singlet, Fl); 125.9 (singlet, Fl); 121.1 (singlet, Fl). Principal IR bands (cm^{-1}): 3062 (w), 3046 (w), 2948 (m), 2887 (w), 2817 (m), 1449 (m), 1291 (w), 959 (s), 720 (s). X-ray quality crystals were grown by slow evaporation of a saturated THF solution.

Synthesis of Dimethylbis(fluorenyl)phosphoylide, $Me_2P(FlH)(Fl)$ (II). Method A. I (0.530 g, 1.02 mmol) was slurried in 40 mL of THF with a magnetic stirring bar. KH (0.044 g, 1.1 mmol) was added with stirring. The solution became yellow as gas evolved, and the reaction mixture was stirred overnight to reach completion. The turbid reaction mixture was filtered in order to remove the slight excess of KH and the precipitated KI. The yellow filtrate was placed under vacuum and stripped to dryness, leaving a light yellow solid. It was washed with a minimal amount of hexanes (2 × 5 mL) and dried under vacuum to afford 0.256 g (64%) of $Me_2P(FlH)(Fl)$ (**II**), mp 257 °C. ^1H NMR (THF-d_8): δ 8.08−6.73 (multiplets, 16H, ring Fl); 5.49 (doublet, $J = 18.4$ Hz, 1H, $CH_3PCH(Fl)$); 1.89 (doublet, $J = 12.9$ Hz, 6H, PCH_3). ^{31}P NMR (THF-d_8): δ 10.75. Principal IR bands (cm^{-1}): 3071 (sh), 3046 (w) 2998 (w), 2983 (w), 2960 (w), 2904 (w), 1607 (w), 1583 (w), 1465 (w), 1432 (s), 1325 (w), 1304 (m), 1300 (s), 1213 (m), 1154 (w), 1121 (m), 1022 (m), 1006 (s), 922 (s), 783 (w), 748 (s), 736 (s), 718 (s), 494 (m).

Method B. I (0.375 g, 0.723 mmol) was slurried in 60 mL of toluene with a magnetic stirring bar. $K[N(SiMe_3)_2]$ (0.144 g, 0.722 mmol) was added, and the initially cloudy mixture became increasingly yellow as stirring continued. After 2 h, the nearly transparent solution was filtered, and the solvent was removed from the filtrate under vacuum to afford a light yellow powder. The powder was washed with a minimal amount of hexanes (10 mL) and dried (0.22 g, 78% yield). Analysis of the ^1H and ^{31}P NMR spectra indicated that the product was identical to that obtained by method A.

Synthesis of Potassium Dimethylbis(fluorenyl)phosphodiylide, $K[Me_2P(Fl)_2]$. I (0.365 g, 0.704 mmol) was added to a flask containing a magnetic stirring bar and 40 mL of THF. KH (0.086 g, 2.1 mmol) was added, and the slurry was stirred overnight. During this time the mixture became light orange and gas evolved. The cloudy solution was filtered through a medium-porosity frit to remove insoluble material (KI and excess KH). The light orange filtrate was stripped to dryness under vacuum and washed with small amounts (2 × 10 mL) of toluene. The solid was then dried under vacuum to yield light orange $K[Me_2P(Fl)_2]$ (0.231 g, 77%), mp 310 °C (dec). Satisfactory elemental analysis could not be obtained. ^1H NMR (THF-d_8): δ 7.99 (doublet, $J = 7.6$ Hz, 4H, ring Fl); 7.49 (doublet, $J = 8.1$ Hz, 4H, ring Fl); 6.89 (triplet, $J = 8.1$ Hz, 4H, ring Fl); 6.74 (triplet, $J = 7.5$ Hz, 4H, ring Fl); 3.62 (singlet (br), 20H, α-C_4H_8O); 2.41 (doublet, $J = 9.0$ Hz, 6H, PCH_3), 1.77 (singlet (br), 20H, β-C_4H_8O). ^{31}P NMR (THF-d_8): δ −9.2. ^{13}C NMR (THF-d_8): δ 141.3 ($CH_3PCH(Fl)$); 141.1 (CH_3−P); 129.7 (ring Fl); 129.1 (ring Fl); 128.9 (ring Fl); 126.0 (ring Fl); 122.7 (ring Fl); 119.8 (ring Fl); 116.5 (ring Fl); 113.8 (ring Fl); 66.8 (α-C_4H_8O); 24.8 (β-C_4H_8O).

Synthesis of Calcium Iodide Pentakis(tetrahydrofuranate) Dimethylbis(fluorenyl)phosphodiylide, $[CaI(thf)_5][Me_2P(Fl)_2]$ (III). Method A. I (0.163 g, 0.314 mmol) was added to a flask containing a magnetic stirring bar and 40 mL of THF. Calcium bis(hexamethyldisilazide) (0.114 g, 0.316 mmol) was added to the slurry, which immediately became yellow. Stirring was continued for 30 min, by which time the solution had become homogeneous. The THF was removed under vacuum to yield an orange oil. The oil was washed with a minimal amount of toluene (2 × 15 mL), and the residue was dried under vacuum. The solid was redissolved in THF and placed in one side of an H-tube. The opposite side of the H-tube was charged with hexanes, and the tube was left undisturbed. After approximately 1 week, X-ray quality crystals had grown, and they were removed by filtration for analysis. The remaining filtrate was placed under vacuum to remove the solvent, leaving 0.096 g (33%) of $[CaI(thf)_5][Me_2P(Fl)_2]$ (**III**), mp 261−265 °C (dec). Anal. Calcd for $C_{48}H_{62}CaIO_5P$: C, 62.87; H, 6.82; Ca, 4.37; P, 3.38. Found: C, 60.33; H, 6.24; Ca, 4.21; P, 3.07. ^1H NMR (C_6D_6): δ 8.31 (doublet, $J = 7.8$ Hz, 4H, ring Fl); 7.83 (doublet, $J = 7.7$ Hz, 4H, ring Fl); 7.38 (triplet, $J = 7.7$ Hz, 4H, ring Fl); 7.21 (triplet, $J = 7.8$ Hz, 4H, ring Fl); 3.31 (singlet (br), 20H, α-C_4H_8O); 1.84 (doublet, $J = 13.2$ Hz, 6H, PCH_3), 1.16 (singlet (br), 20H, β-C_4H_8O). ^1H NMR (THF-d_8): δ 7.93 (doublet, $J = 7.5$ Hz, 4H, ring Fl); 7.45 (doublet, $J = 8.1$ Hz, 4H, ring Fl); 6.81 (triplet, $J = 8.1$ Hz, 4H, ring Fl); 6.65 (triplet, $J = 7.5$ Hz, 4H, ring Fl); 3.53 (singlet (br), 20H, α-C_4H_8O); 2.35 (doublet, $J = 9.0$ Hz, 6H, PCH_3), 1.70 (singlet (br), 20H, β-C_4H_8O). ^{31}P NMR (C_6D_6): δ −7.7. ^{31}P NMR (THF-d_8, 20 °C): δ −10.5. ^{13}C NMR (C_6D_6, 20 °C): δ 139.6 (CH_3−P); 129.3 (ring Fl); 120.6 (ring Fl); 115.9 (ring Fl); 114.8 (ring Fl); 68.5 (α-C_4H_8O); 25.1 (β-C_4H_8O). ^{13}C NMR (THF-d_8): δ 141.5 (CH_3−P); 128.8 (ring Fl); 124.2 (ring Fl); 121.9 (ring Fl); 119.0 (ring Fl); 117.1 (ring Fl); 113.1 (ring Fl); 68.2 (α-C_4H_8O); 26.2 (β-C_4H_8O). Principal IR bands (cm^{-1}): 3036 (m), 2964 (m), 2912 (w), 2870 (w), 1603 (w), 1575 (w), 1460 (m), 1427 (s), 1300 (s), 1217 (m), 1114 (s), 1018 (s), 802 (w), 752 (m), 722 (m), 462 (m). Crystals used for X-ray analysis were found to have an additional THF molecule in the lattice.

Method B. I (0.532 g, 1.03 mmol) was placed in a medium Schlenk flask and slurried in THF (200 mL). On a Schlenk line, 0.83 mL of a 2.5 M solution of *n*-BuLi (2.1 mmol) was added dropwise. The solution became increasingly yellow and more homogeneous as the addition progressed, and it became uniform after the addition was completed. Stirring of the light orange solution was continued for 1 h. CaI_2 (0.302 g, 1.03 mmol) was placed in a separate Schlenk flask and was dissolved in THF (50 mL). The dilithio salt solution was slowly cannulated into the calcium iodide solution, and the mixture was stirred for 12 h, during which time it faded slightly in color. The solvent was removed under vacuum, leaving a brown gummy oil. A minimal amount of hexanes (2 × 10 mL) was added, removed shortly thereafter as a light yellow solution by filtration, and discarded. Toluene (50 mL) was added to the residue, and the resulting mixture was separated by filtration over a medium-porosity frit to afford a dark orange filtrate. The latter was cooled to −20 °C. After 12 h, an oil separated from the toluene solution and was isolated by removal of the toluene by cannulation. Upon placing the oil under vacuum, it solidified into a wax. The remaining toluene solution was evaporated to a solid; both it and the wax were analyzed by ^1H and ^{31}P NMR and were found to contain **III**.

Synthesis of Barium Iodide Pentakis(tetrahydrofuranate) Dimethylbis(fluorenyl)phosphodiylide, $[BaI(thf)_5][Me_2P(Fl)_2]$. Method A. In a manner similar to that used for **III**, barium bis(hexamethyldisilazide) (0.143 g, 0.314 mmol) was added to a slurry of **I** (0.163 g, 0.314 mmol) in THF (40 mL). Workup as before left an orange oil, which was washed with a minimal amount of toluene (2 × 15 mL), and the remaining solid was dried under vacuum. After 36 h, the oil began to crystallize and ultimately formed a wax (0.122 g, 38%), mp 125−135 °C. Possibly owing to the semisolid nature of the material, and its desolvation on heating to form an oil, satisfactory elemental analysis could not be obtained for this compound. ^1H NMR (C_6D_6): δ 8.31 (doublet, $J = 7.8$ Hz, 4H, ring Fl); 7.83 (doublet, $J = 7.7$ Hz, 4H, ring Fl); 7.38 (triplet, $J = 7.7$ Hz, 4H, ring Fl); 7.21 (triplet, $J = 7.8$ Hz, 4H, ring Fl); 3.43 (singlet (br), 20H, α-C_4H_8O); 1.84 (doublet, $J = 13.2$ Hz, 6H, PCH_3), 1.20 (singlet (br), 20H, β-C_4H_8O). ^1H NMR (THF-d_8): δ 7.93 (doublet, $J = 7.5$ Hz, 4H, ring Fl); 7.45 (doublet, $J = 8.1$ Hz, 4H, ring Fl); 6.80 (triplet, $J = 6.9$ Hz, 4H, ring Fl); 6.65 (triplet, $J = 7.5$ Hz, 4H, ring Fl); 3.63 (multiplet (br), ∼20H, α-C_4H_8O); 2.35 (doublet, $J = 12.6$ Hz, 6H, PCH_3), 1.76 (multiplet (br), 20H, β-C_4H_8O). ^{31}P NMR (C_6D_6): δ −7.7. ^{31}P NMR (THF-d_8): δ −10.5. ^{13}C NMR (C_6D_6, 20 °C): δ 139.6 (CH_3−P); 129.3 (ring Fl); 120.6 (ring Fl); 115.9 (ring Fl); 114.8 (ring Fl); 68.5 (α-C_4H_8O); 25.1 (β-C_4H_8O). ^{13}C NMR (THF-d_8): δ 141.5 (CH_3−P); 128.8 (ring Fl); 124.2 (ring Fl); 121.9 (ring Fl); 119.0 (ring Fl); 117.1 (ring Fl); 113.1 (ring Fl); 68.2 (α-C_4H_8O); 26.2 (β-C_4H_8O). Principal IR bands (cm^{-1}): 3045

Table 1. Crystal Data and Summary of X-ray Data Collection

formula	$C_{28}H_{24}IP$	$C_{28}H_{23}P$	$C_{52}H_{70}CaIO_6P$
fw	518.38	390.46	989.08
color of cryst	colorless	yellow	yellow
cryst dimens (mm)	0.32 × 0.2 × 0.12	0.45 × 0.04 × 0.04	0.32 × 0.28 × 0.25
space group	$P2/c$	$P2_1/c$	$P2_1/n$
a (Å)	7.3318(1)	9.7330(7)	13.0619(7)
b (Å)	10.1580(1)	17.8237(12)	22.64197(13)
c (Å)	14.8414(3)	12.3659(8)	17.9082(10)
β (deg)	94.972(1)	110.621(1)	110.658(1)
vol (Å^3)	1101.18(3)	2007.8(2)	4955.7(5)
Z	2	4	4
density (calcd) (Mg m^{-3})	1.563	1.292	1.326
abs coeff (mm^{-1})	1.540	0.149	0.829
F(000)	520	824	2072
radiation type (λ)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
temp (K)	173(2)	173(2)	173(2)
limits of data collection	$2.00° \le \theta \le 24.97°$	$2.10° \le \theta \le 25.04°$	$2.50° \le \theta \le 25.04°$
index ranges	$-8 \le h \le 8$, $0 \le k \le 12$, $0 \le l \le 17$	$-11 \le h \le 10$, $0 \le k \le 21$, $0 \le l \le 14$	$-16 \le h \le 15$, $0 \le k \le 29$, $0 \le l \le 23$
total reflcns collected	5585	10376	38232
unique reflcns	1928 ($R_{int} = 0.0185$)	3542 ($R_{int} = 0.0362$)	11257 ($R_{int} = 0.0325$)
weighting scheme^a	$A = 0.0320$, $B = 0.5192$	$A = 0.0627$, $B = 0.0$	$A = 0.0604$, $B = 0.266$
transmn factors	0.878−1.000	0.7474−1.000	0.737−1.000
data/restraints/params	1928/0/185	3542/0/264	11257/548/596
R indices ($I > 2\sigma(I)$)	R1 = 0.0207, wR2 = 0.0538	R1 = 0.0442, wR2 = 0.1041	R1 = 0.0408, wR2 = 0.1033
R indices (all data)	R1 = 0.0256, wR2 = 0.0555	R1 = 0.0714, wR2 = 0.1132	R1 = 0.0747, wR2 = 0.1152
goodness of fit on F^2	1.012	0.994	1.040
largest diff peak and hole (e/Å^3)	0.306, −0.484	0.334, −0.409	0.782, −0.684

^{a} $w = [\sigma^2(F_o{}^2) + (AP)^2 + (BP)]^{-1}$, where $P = (F_o{}^2 + 2F_c{}^2)/3$.

(w), 2960 (m), 2903 (w), 2872 (w), 1605 (w), 1574 (w), 1428 (m), 1310 (m), 1216 (w), 1107 (m), 1086 (m), 1037 (s), 913 (m), 796 (w), 473 (w).

Method B. As with the second procedure described for **III** above, $[Me_2P(FlLi)_2]I$ (0.550 g, 1.04 mmol) was prepared in situ in a medium Schlenk flask. BaI_2 (0.406 g, 1.03 mmol) was placed in a separate Schlenk flask and was dissolved in THF (50 mL). The dilithio salt solution was slowly cannulated into the barium iodide solution, and stirring of the solution was continued for 12 h. Workup as before left a dark reddish-orange solution, which became a red oil on removal of toluene. On prolonged standing, the oil solidified into a wax. The wax was analyzed with ^1H and ^{31}P NMR and was found to contain the same material obtained with method A.

Computational Details. Calculations were performed using Gaussian 98W.[27] Geometry optimizations were carried out with the B3PW91 functional, which incorporates Becke's three-parameter exchange functional[28] with the 1991 gradient-corrected correlation functional of Perdew and Wang.[29] The standard 6-31+G(d) basis set was used for all calculations; a trial optimization of $[H_2P(CH_2)_2]^-$ with the larger 6-311+G(2d,p) basis set made negligible differences in bond lengths (<0.01 Å) and angles (<0.5°). Stationary points were characterized by the calculation of vibrational frequencies, and all final geometries were found to be minima (zero imaginary frequencies). Atomic charges were calculated with the natural population analysis method.[30,31]

General Procedures for X-ray Crystallography. A suitable crystal of each sample was located, attached to a glass fiber, and mounted on a Siemens SMART system for data collection at 173(2) K. Data collection (SAINT: Siemens Industrial Automation, Inc, Madison, WI) and structure solution were conducted at the X-ray Crystallography Laboratory at the University of Minnesota. All calculations were performed using SGI INDY R4400-SC or Pentium computers using the SHELXTL V5.10 suite of programs (SHELXTL-Plus V5.1, Siemens Industrial Automation, Inc., Madison, WI). Final cell constants were calculated from a set of strong reflections measured during the actual data collection. Relevant crystal and data collection parameters for each of the compounds are given in Table 1.

The space groups were determined from systematic absences and intensity statistics. A direct-methods solution was calculated that provided most non-hydrogen atoms from the *E*-map. Several full-matrix least-squares/difference Fourier cycles were performed that located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Absorption corrections were performed with the program SADABS (SADABS: Area-Detector Absorption Correction; Siemens Industrial Automation, Inc.: Madison, WI, 1996).

Results

Ligand Syntheses. The reaction of $MePCl_2$ with either lithium or potassium fluorenide in a mixture of Et_2O and hexanes produces methylbis(fluorenyl)phosphine ($MeP(FlH)_2$) in good (83%) yield. This reaction is performed at reduced temperatures (−40 °C); if the reaction is conducted at ambient temperature, the product is obtained in lower yield. The neutral phosphine is only sparingly soluble in ether and toluene, but it has good solubility in CH_2Cl_2, which proved to be instrumental in separating it from the LiCl byproduct. It is stable in water for hours, but converts cleanly into the corresponding phosphine oxide $Me(O)P(FlH)_2$ if left in air for 48 h.

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When $\mathrm{MeP(FlH)_2}$ is slurried in a flask with THF and allowed to react with methyl iodide overnight (eq 1), the solution

$$\mathrm{MeP(FlH)_2 + MeI \xrightarrow{THF} \underset{\textbf{I}}{[Me_2P(FlH)_2]I}} \tag{1}$$

becomes increasingly cloudy as the reaction progresses. The white phosphonium iodide salt (**I**) can be isolated in good (73%) yield. It is deprotonated with 1 equiv of KH in THF to yield the corresponding pale yellow neutral ylide $\mathrm{Me_2P(FlH)(Fl)}$ (**II**).

NMR analysis (^{1}H, ^{13}C, and ^{31}P) reveals distinctive shifts for the methyl protons and phosphorus centers in these compounds. The ^{1}H NMR of the neutral phosphine ($\mathrm{MeP(FlH)_2}$) displays a broad singlet at 4.66 ppm that is assigned to the allylic proton on the fluorenyl ring and a doublet from the methyl protons at 0.47 ppm. In the phosphonium iodide (**I**), the ^{1}H peaks corresponding to the allylic protons move downfield to 5.46 ppm and resolve into a doublet. The methyl protons also shift downfield from 0.47 to 2.03 ppm; this is expected on the basis of known spectra of phosphines and their related phosphonium salts.[32] The ^{31}P peak in **I** (36.0 ppm) is shifted downfield from that of the neutral phosphine (−2.2 ppm). In **II**, the remaining allylic proton on one of the fluorenyl rings is found in the ^{1}H NMR spectrum at 5.49 ppm, and the doublet for the methyl protons is at 1.89 ppm; the ^{31}P peak appears at 10.7 ppm.

Potassium dimethylbis(fluorenyl)phosphodiylide ($\mathrm{K[Me_2P(Fl)_2]}$) is available by using 2 equiv of KH (or $\mathrm{K[N(SiMe_3)_2]}$) with **I**; 1 mol of KI and 2 mol of $\mathrm{H_2}$ gas (or $\mathrm{HN(SiMe_3)_2}$) are the byproducts. The ^{1}H NMR spectrum for the potassium complex is consistent with the formation of a diylide, as there are no resonances in the allylic region, and the fluorenyl resonances are more symmetrical, a reflection of the higher symmetry of the ligand. The doublet for the methyl protons shifts to 2.41 ppm, and the ^{31}P resonance moves to −9.2 ppm.

Interaction with Alkaline-Earth Metals. The bis(hexamethyldisilazide) salts of the alkaline-earth metals possess excellent solubility in aromatic solvents.[25,26] We have found that reaction of 2 equiv of $\mathrm{K[N(SiMe_3)_2]}$ with any of the heavy alkaline-earth (Ae) diiodides in toluene (eq 2) proceeds in good to

$$\mathrm{AeI_2 + 2K[N(SiMe_3)_2] \xrightarrow[-2KI]{toluene} Ae[N(SiMe_3)_2]_2} \tag{2}$$

excellent yields for the alkaline-earth complexes. We have been dissatisfied with the quality of commercial sources of potassium hexamethyldisilazide, and we synthesize it in situ from the free amine ($\mathrm{H[N(SiMe_3)_2]}$) and KH in a glovebox. Once gas evolution ceases, the mixture is filtered to remove excess KH and any other impurities present prior to addition of an alkaline-earth diiodide. Yields are critically dependent on the quality of the potassium salt; if it is not freshly prepared, production of the alkaline-earth derivatives drops to 20% or less.

The neutral phosphine $\mathrm{MeP(FlH)_2}$ was allowed to react with each of the alkaline-earth bis(hexamethyldisilazides) in THF. In each case, a dark red, moisture-sensitive solid immediately precipitates from THF (Scheme 2). As the solids are insoluble in all conventional solvents, NMR data is not available; the free amine ($\mathrm{HN(SiMe_3)_2}$), however, is detected as a product of the reaction by ^{1}H NMR in THF-d_8. Elemental analysis was unsatisfactory for these solids, although they are possibly the alkaline-earth complexes of the dinegative phosphine ligand, i.e., $\mathrm{(MeP(Fl)_2)Ae(thf)}_n$.

The addition of $\mathrm{Ca[N(SiMe_3)_2]_2}$ to a slurry of the phosphonium iodide (**I**) in THF immediately generated a yellow color. Upon isolation of the product, no allylic protons from the fluorenyl rings of the starting material were present in the ^{1}H NMR spectrum, and the ^{31}P NMR signal had moved upfield from 36.0 ppm in **I** to −7.7 ppm. A similar reaction with barium bis(hexamethyldisilazide) provided nearly identical ^{1}H and ^{31}P NMR spectra. An X-ray diffraction study performed on suitable crystals of the calcium compound (**III**) found that the phosphodiylide was uncomplexed, and the calcium ion was incorporated in a solvated mono(iodo) cation $\mathrm{[CaI(thf)_5]^+}$ (see below). Evidently, the calcium starting material loses both amido ligands during the deprotonation of the fluorenyl groups, and appropriates the iodide from the phosphonium salt. Crystals of the waxy barium analogue could not be obtained for comparison.

Treatment of **I** with 2 equiv of *n*-BuLi afforded the dilithio salt (Scheme 2). The salt was not isolated, but was instead allowed to react in situ with $\mathrm{AeI_2}$ in the appropriate stoichiometry. Analysis with ^{1}H and ^{31}P NMR spectra indicated that the product of the reaction was also $\mathrm{[AeI(thf)_5][Me_2P(Fl)_2]}$.

In order to determine whether THF was materially changing the course of the reactions, additional experiments were run in toluene; this led to the isolation of the crystalline phosphoylide **II** along with insoluble products (eq 3).

$$\mathrm{[Me_2P(FlH)_2]I + Ae[N(SiMe_3)_2]_2 \xrightarrow{toluene} Me_2P(FlH)(Fl) + byproducts} \tag{3}$$

Precipitation of KI is ordinarily an effective driving force in heavy alkaline-earth organometallic and coordination chemistry,[1,33] but the mono(iodo) cations are unreactive toward substitution with KCp*, and starting materials were recovered after an attempted reaction (eq 4).

$$\mathrm{[AeI(thf)_5][Me_2P(Fl)_2] + KCp^* \xrightarrow{THF} NR} \tag{4}$$

Solid State Structures

Solid-State Structure of $\mathrm{[Me_2P(FlH)_2]I}$. A crystal of **I** was isolated from a saturated THF solution and used to determine its structure by X-ray diffraction. The structure is composed of stacked layers of the substituted phosphonium cations interspersed with iodide anions. The methyl and fluorenyl groups are in a distorted tetrahedral arrangement around the phosphorus atom, with the individual $\mathrm{[Me_2P(FlH)_2]^+}$ cations linked by long H bonds to the iodides (Figure 1). Crystallographically imposed C_2 axes pass through both the iodine and phosphorus atoms, and the two methyl groups and fluorenyl rings in each molecule are equivalent. The P−C(ipso) bond (1.837(2) Å) is marginally longer than the $\mathrm{P{-}CH_3}$ distance (1.794(2) Å); this is similar to the order observed in the dimethyldiphenylphosphonium iodide $\mathrm{[Me_2PPh_2]I}$ (1.794(5) Å ($\mathrm{P{-}C_6H_5}$) and 1.764(4) Å ($\mathrm{P{-}CH_3}$)).[34]

The plane defined by the two methyl groups and P atom (C14−P1−C14′) is roughly perpendicular (83.3°) to the plane defined by the two *ipso*-C atoms of the fluorenyl groups and the P atom (C1−P1−C1′). In contrast, the angle between the C1−P1−C1′ plane and the least-squares plane through the fluorenyl moiety is 69.0°, so there is a pronounced tilt to the arrangement of the substituents on the phosphorus (Figure 2).

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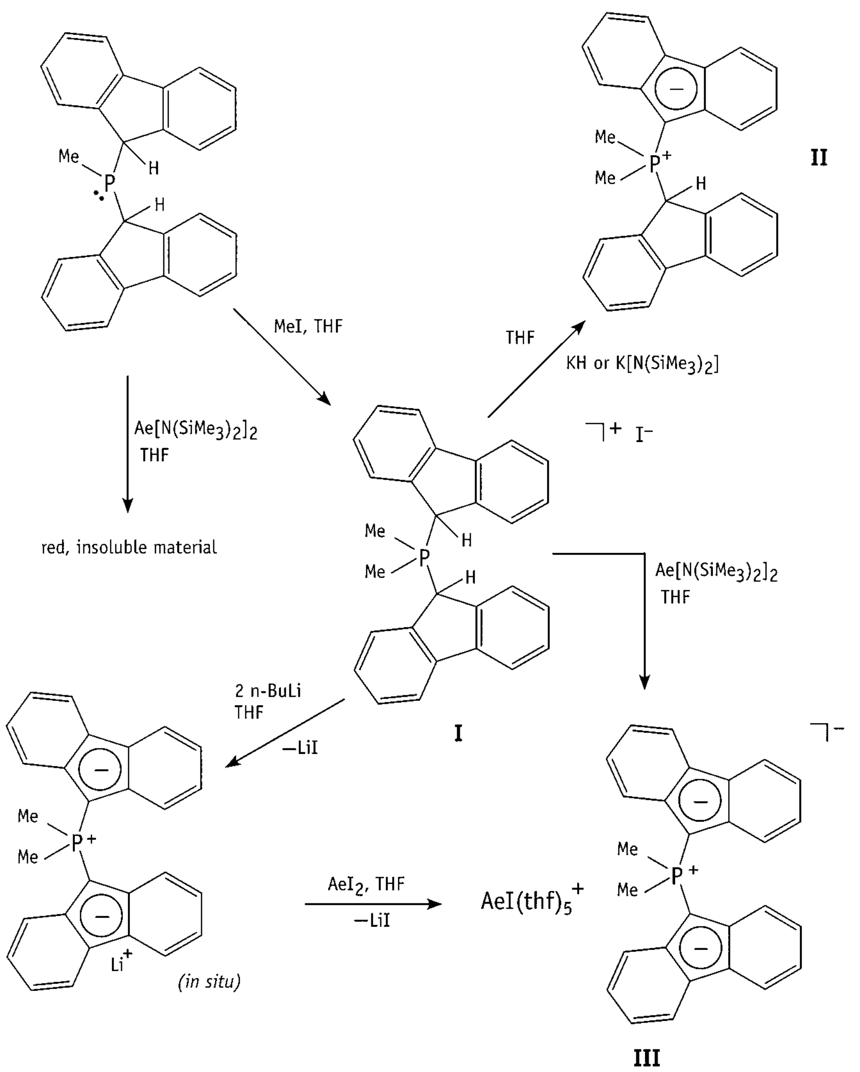
Scheme 2. Summary of Reactions Involving $[Me_2P(FlH)_2]I$ (**I**)



There is probably significant π-interaction between the rings, as indicated by the intermolecular fluorenyl ring spacing of approximately 3.50 Å (cf. the intramolecular ring separation of 3.33 Å), and by the small dihedral angle between the fluorenyl ring planes: only 6.1° (intramolecular) and 5.6° (intermolecular).[35] In addition, the iodide ions are coordinated by a highly distorted octahedral array of contacts with hydrogen atoms on the methyl groups and the fluorenyl rings at distances extending from 3.09 to 3.24 Å. The $[Me_2PPh_2]I$ structure contains similar iodide−hydrogen contacts at 3.05 and 3.17 Å.[34] These distances are near the sum of the van der Waals radii for H and I (∼3.3 Å)[36] and are probably responsible for the angular distortions in the cations and their relatively tight packing. The latter may contribute to the near insolubility of **I** in ethereal and aromatic solvents; the other fluorenyl derivatives (neutral or charged) used in this study are generally much more soluble.

Solid-State Structure of $Me_2P(FlH)(Fl)$. A needle of **II** was isolated from a saturated THF solution and used for the X-ray structure determination. The phosphorus is in a distorted tetrahedral environment generated by the two methyl groups, the fluorenyl ring (ring A), and the fluorenylidene ring (ring B) (Figure 3). It is only the second structurally authenticated phosphonium fluorenylide to be reported.[37]

The methyl−phosphorus bond lengths are equivalent (1.798(2) and 1.795(2) Å), but the P−C(ring) distances are unequal. The P(1)−C(3) distance (1.847(2) Å) (cf. 1.837(2) Å in **I** and 1.833(10) Å in PPh_3[38]) is appropriate for a P−C single bond, and the P(1)−C(16) distance (1.724(2) Å) (cf. 1.718(2) Å in $Ph_3P{=}C_5H_4$[39] and 1.698(7) Å in $[(i\text{-Pr})_2N]_2P(Cl){=}$fluorenylidene)[37] reflects the partial ylene character of the interaction.[40] The phosphorus atom lies 0.255 Å out of the least-squares plane defined by the C_5 ring (C16, C17, C22, C23, C28), which leads to an angle of 171.5° between the P(1)−C(16) vector and the ring. The angle between P(1)−C(3) and the central C_5 ring in the A ring is 111.1°, as expected for substituents on an sp^3-hybridized carbon atom.

The B ring is nearly planar, with an angle between the two C_6 benzo rings of 4.0°. In contrast, the A ring is markedly bent; the benzo rings form an angle of 15.0° with respect to each other. This may be partially a consequence of close packing effects, as there are several intermolecular C−C and C−H contacts involving the A ring that are at or below the sum of

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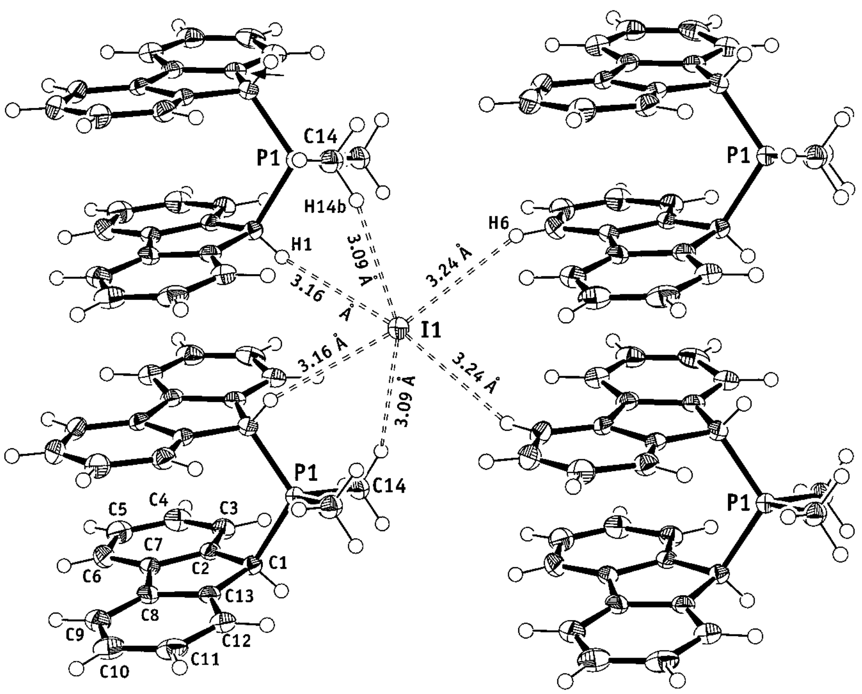

Figure 1. ORTEP diagram of $[Me_2P(FlH)_2]I$ (**I**), giving the numbering scheme used in the text. The structure also shows the close contacts around a centrally located iodide. Thermal ellipsoids are shown at the 30% level.

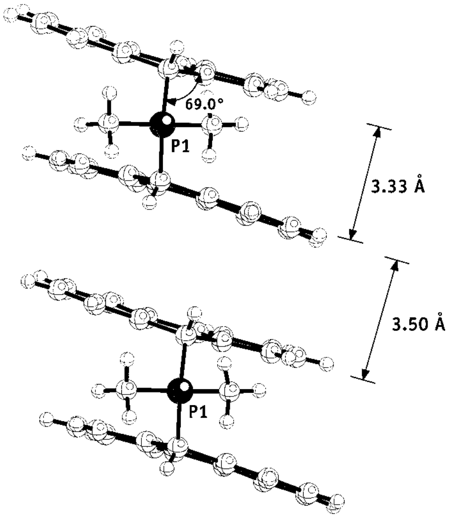

Figure 2. Tilting of the C1−P1−C1′ plane relative to the fluorenyl plane in **I**, and the intra- and intermolecular ring spacing.

their respective van der Waals radii of 3.4 and 2.9 Å (i.e., C14−C28′ = 3.36 Å; C14−C27′ = 3.37 Å; H3A−C17′ = 2.56 Å; H3A−C22′ = 2.58 Å).

Solid-State Structure of $[CaI(thf)_5][Me_2P(Fl)_2]$. A crystal of **III** was grown from a THF solution as described in the Experimental Section. The structure consists of discrete six-coordinate thf-solvated calcium mono(iodide) cations and phosphonium bifluorenylide anions (Figure 4). A THF in the lattice completes the structure. To the best of our knowledge, this represents the first structurally authenticated example of an uncomplexed phosphonium diylide.

Several parameters can be used to define the environment about phosphorus (Table 2). Diylides display a characteristic angle between the R_2P and PC_2 planes that has its origin in negative hyperconjugation between the ylidic carbon “lone pair” and the π^* orbital on the PR_2 moiety; its magnitude is a function of the ylene character of the P−C bond.[20,41] In $[H_2P(CH_2)_2]^-$, for example, the R_2P/PC_2 angle is calculated to be 71.5° (Table 3). In contrast, the Me_2P and PC_2 planes in **III** are nearly perpendicular (87.2°). The fluorenylidene rings differ sharply with respect to their orientation to the C(ring)−P−C(ring) plane: that which contains C3 forms an angle of 12.7° with the plane; the ring that contains C16 is tilted by 69.3° from the C−P−C′ plane in the opposite direction, so that the two fluorenylidene moieties form an approximate 82° angle with each other. The wide angle between the rings is larger than that calculated for the $[Me_2P(C_5H_4)_2]^-$ anion (see below), which might indicate some steric interaction between them or the operation of crystal packing forces between the cations and

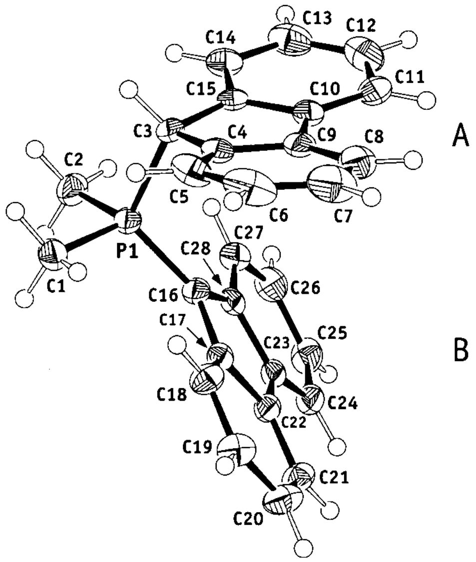

Figure 3. ORTEP diagram of $Me_2P(FlH)(Fl)$ (**II**), giving the numbering scheme used in the text. The fluorenyl ring is designated “A”, and the fluorenylidene ring is labeled “B”. Thermal ellipsoids are shown at the 50% level.

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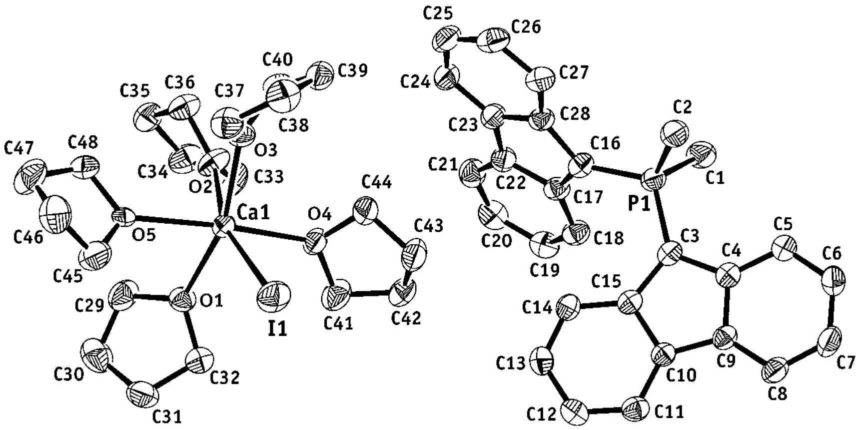

Figure 4. ORTEP diagram of the non-hydrogen atoms of $[CaI(thf)_5][Me_2P(Fl)_2]$, giving the numbering scheme used in the text. Thermal ellipsoids are shown at the 50% level.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[CaI(thf)_5]$ $[Me_2P(Fl)_2]$

atoms	distance	atoms	angle
P(1)−C(1)	1.812(3)	C(16)−P(1)−C(2)	110.57(13)
P(1)−C(2)	1.797(3)	C(16)−P(1)−C(1)	108.39(14)
P(1)−C(3)	1.750(3)	C(16)−P(1)−C(3)	115.72(13)
P(1)−C(16)	1.746(3)	C(2)−P(1)−C(1)	103.0(2)
Ca(1)−I(1)	3.0679(6)	C(2)−P(1)−C(3)	109.75(13)
Ca(1)−O(av)	2.35	C(1)−P(1)−C(3)	108.60(13)
		O(4)−Ca(1)−O(5′)	175.7(6)
		O(2)−Ca(1)−I(1)	163.50(6)

anions (e.g., C25 and C46′ are separated by 3.37 Å; C1 and C19′ are separated by 3.50 Å).

The P(1)−C(16) and P(1)−C(3) bond lengths (1.746(3) and 1.750(3) Å, respectively) reflect some double-bond character and are comparable to the P−fluorenylidene distance found in **II** (1.742(2) Å). The double-bond character is also evidenced in the wide angles between the P(1)−C(16) and P(1)−C(3) bond vectors and the associated fluorenyl ring planes (169.3° and 177.8°, respectively); the sum of the angles around C(16) (358.2°) and C(3) (359.7°) indicates the near planarity of the ylidic carbons.

The Ca−I distance of 3.0679(6) Å is only slightly shorter than that found in other six-coordinate calcium species, such as $CaI_2(thf)_4$ (3.106(2) Å),[42,43] $CaI_2(H_2O)_4$ (3.127(7) Å),[44] and $CaI_2(bipy)_2$ (3.078(1) Å).[45] Group 2−iodide bond distances and angles do not correlate well with metal coordination number or the terminal/bridging arrangement of the iodide,[3] so the lack of a larger effect from the charge on the complex is not surprising. The Ca−O(thf) contacts (av 2.35 Å) are also typical for neutral oxygen donors, cf. 2.34(1) Å in $CaI_2(thf)_4$[42] and 2.309(8) Å in $CaI_2(H_2O)_4$.[44]

Computational Results

Phosphonium ylides have been repeatedly examined with semiempirical and ab initio (HF) computational methods, some of which include corrections for electron correlation.[40,46−48] Phosphonium *di*ylides have received less attention and have not been studied with density functional theory (DFT) approaches, which provide an accounting for electron correlation effects.[49−51] Harder examined the $[H_2P(CH_2)_2]^-$ and $[H_2P(CHPh)_2]^-$ diylides at the HF/6-31+G(d) level and used NPA charges to investigate the degree of charge delocalization in the molecules.[20] For comparison, we recalculated $[H_2P(CH_2)_2]^-$ with the B3PW91/6-31+G(d) combination and also examined $[Me_2P(CH_2)_2]^-$ and $[Me_2P(C_5H_4)_2]^-$; the latter was used as a model for $[Me_2P(C_{13}H_8)_2]^-$. Drawings of the optimized geometries of the molecules are provided in Figure 5; key distances and angles are summarized in Table 3.

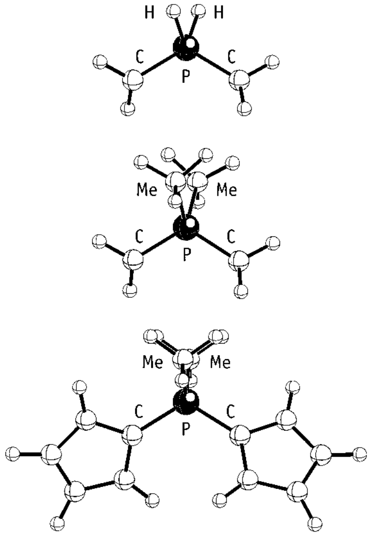

Figure 5. Calculated geometries (B3PW91/6-31+G(d)) of phosphonium diylides. The angle between the R−P−R (R = H, Me) and C(ylidic)−P−C(ylidic) planes decreases as the substituents on the ylidic carbon are varied from H to Me to C_5H_4 (the paper contains the Me−P−Me plane).

The dimethylphosphonium bis(cyclopentadienylide) was originally examined as a more computationally tractable version of the larger fluorenylide-containing diylide, but the metrical parameters of the optimized geometry of $[Me_2P(C_5H_4)_2]^-$ match

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Table 3. Calculated Structures of Phosphonium Diylides[a]

compound	computational level	P=C	C=P=C	R_2P/PC_2[b]	ref
$[H_2P(CH_2)_2]^-$	HF/6-31+G(d)	1.705	117.9	74.4	20
$[H_2P(CH_2)_2]^-$	B3PW91/6-31+G(d)	1.710	117.3	71.5	this work
$[H_2P(CH_2)_2]^-$	B3PW91/6-311+G(2d,p)	1.704	117.2	72.5	this work
$[H_2P(CHPh)_2]^-$	HF/6-31+G(d)	1.717	115.5	78.3	20
$[Me_2P(CH_2)_2]^-$	B3PW91/6-31+G(d)	1.714	115.5	77.8	this work
$[Me_2P(C_5H_4)_2]^-$	B3PW91/6-31+G(d)	1.746	115.9	86.6	this work
$[Me_2P(C_{13}H_8)_2]^-$	exptl (X-ray)	1.748(4) (av)	115.7	87.2	this work

[a] Distances are in Å; angles are in degrees. [b] Angle between the R−P−R (R = H, Me) and C(ylidic)−P−C(ylidic) planes.

those in the crystallographically characterized **III** to a remarkable degree. These values include the P−C distance (1.748(4) Å (obs) (cf. 1.746 Å (calc)), the C−P−C′ angle (106.8(3)° (obs) (107.7° (calc)), and the narrow spread of C−C bond lengths in the C_5 ring (0.020 Å (obs) (0.034 Å (calc)). It should also be noted that the computed structure of the free anion is not greatly different from that of the substituted, complexed [Me$_2$P(2-Me-4-*t*-BuC$_5$H$_2$)$_2$]$^-$ anion;[21] e.g., the P−C distances in the potassium and barium derivatives average to 1.751 and 1.746 Å, respectively. The C−P−C′ angle in the two complexes does open slightly to accommodate the metals: in the K complex, the angle is 112.8(4)°; in the Ba compound, the angle is 109.5(2)°.

The rings are more twisted with respect to each other in **III** than in the calculated structure. In **III**, the rings approach perpendicularity (interplanar angle = 81.8°), whereas in the calculated structure, the rings are tipped from the plane by 31.4° and 32.9° in opposite directions, so that the angle between them is 64.3°.

The NPA charges on the R_2P group relative to the rest of the molecule have been taken as a measure of the amount of delocalization in a diylide.[20] For $[H_2P(CH_2)_2]^-$, the H_2P/CH_2 difference of +0.92/−0.96 ($\Delta = 1.88$) that was computed at the HF/6-31+G(d) level[20] is reduced somewhat in the DFT calculation to +0.75/−0.87 ($\Delta = 1.62$). Replacing the hydrogens on the phosphorus with methyl groups leads to the slightly larger Me_2P/CH_2 difference of +0.79/−0.90 ($\Delta = 1.69$). In $[Me_2P(C_5H_4)_2]^-$, the Me_2P/C_5H_4 difference is +1.16/−1.08 ($\Delta = 2.24$); this amount of charge buildup is similar to that previously found for $[H_2P(CHPh)_2]^-$ (+1.09/−1.04; $\Delta = 2.13$)[20] and presumably reflects a similar loss of charge delocalization.

Discussion

Fluorene is often considered an analogue of cyclopentadiene, but the benzo moieties perturb the bonding in such a way that metals rarely exhibit symmetric η^5-binding to two fluorenyl rings.[52,53] In $(Fl)_2Ba(NH_3)_4$, for example, one ring is bound in an η^5 manner to the barium, and the other is slipped to an η^2 arrangement.[54] The constraints imposed by the bridging atom in an *ansa*-metallocene framework add additional variability to the ligation. Calcium is bound in an η^3 manner to both fluorenyl rings in $Me_2Si(Fl)_2Ca(thf)_3$; the barium analogue ($Me_2Si(Fl)_2Ba(thf)_4$) occurs in two forms in the solid, one in which the barium is bound like calcium (η^3,η^3), and the other in which one ring is not slipped (η^5,η^3).[23] The energy difference between an η^3- and η^5-bound fluorenyl group can be small (estimated to be <6 kJ mol^{-1} in LiFl[55]), and crystal packing forces alone may change the bonding mode in main-group fluorenyl complexes.

Variability in metal hapticity aside, it is notable that a fluorenyl-containing anion such as $[Me_2P(Fl)_2]^-$ ignores the presence of an available cation, such as $[(Ca,Ba)I(thf)_n]^+$, and remains uncomplexed. It is possible that the electron-withdrawing properties of the fluorenylidene groups have reduced the basicity of the ylidic carbons; a similar explanation was thought to be part of reason that the phenyl-substituted ylide $H_3P{=}CPh_2$ is a much weaker donor toward acetylene than is $H_3P{=}CH_2$.[48] This does not appear to be a problem inherent to using a phosphonium-bridged "cyclopentadienyl-like" ligand set, however, as the existence of the potassium and barium complexes of phosphonium-bridged alkylated cyclopentadienes, [R$_2$P(2-Me-4-*t*-BuC$_5$H$_2$)$_2$]$^-$ (R = Me, *n*-Bu), demonstrates.[21] Furthermore, calculations on $[H_3Si(Fl)]^-$ and $[H_3Si(Cp)]^-$ suggest that the bending distortions that would accompany their complexation to metals are of nearly equal energy.[23]

Possible steric interference from the fluorenyl rings could contribute to the disinclination of the diylide to bind to the cation. In crystallographically characterized complexes, R_2P−C(ring) distances are about 0.1 Å shorter than the analogous R_2Si−C lengths,[21,56] and it might be expected that the "fit" of a metal in a phosphonium-bridged cyclopentadienyl-type ligand would be tighter than that in a silyl-bridged species. Steric interference from the phenyl rings was believed to be a contributor to the weak nucleophilicity of $H_3P{=}CPh_2$.[48] There is no obvious reason, however, that this difference need preclude metal binding.

The possibility must also be considered that solvation of the calcium cation has substantially weakened its electrophilic character. THF solvation of the Ca^{2+} ion provides a strong driving force for cyclopentadienyl ring exchange; for example, the reaction of (1,2,4-(SiMe$_3$)$_3$C$_5$H$_2$)CaI(thf) with lithium iodide results in the transfer of the cyclopentadienyl anion to the lithium and the formation of $CaI_2(thf)_n$.[5] In addition, a strong neutral donor such as $OPPh_3$ will displace an iodide from CaI_2 in THF to generate the $[CaI(OPPh_3)_4(thf)]^+$ cation.[57] These examples suggest that the pairing of a heavy alkaline-earth cation to anionic ligands (as AeLL′) may not be energetically competitive with the solvated arrangement $[AeL(S)_n]^+L'$ or even $[Ae(S)_n]^{2+}LL'$ (S = neutral donor ligand).

In its current form, the reaction to prepare the $[Me_2P(Fl)_2]^-$ ion depends on the presence of THF. Attempts to deprotonate the $[Me_2P(FlH)_2]^+$ cation with $Ae[N(SiMe_3)_2]_2$ in toluene result in the formation of the neutral ylide, $Me_2P(FlH)(Fl)$ (eq 3). The THF must assist in the deprotonation of the ylide but then, by forming a highly solvated metal ion, leaves the resulting diylide uncomplexed.

Conclusions

From a reaction that was intended to prepare complexes of the general formula $(Me_2P(Fl)_2)AeI(thf)_n$, the uncomplexed

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phosphonium diylide $[Me_2P(Fl)_2]^-$ was isolated and crystallographically characterized. Density functional theory calculations on the model compound $[Me_2P(C_5H_4)_2]^-$ were able to reproduce the core structural features (P−C bond length and relative Me_2P/PC_2 angle) of the difluorenylide compound, suggesting that they are electronically related.

Despite the strong electrostatic attraction that usually drives metal−ligand binding in highly ionic systems, calcium and barium prefer to remain solvated with neutral oxygen donor ligands rather than coordinate to the anionic diylide. This behavior may be more common than previously thought and could affect synthetic strategies for coordination and organometallic complexes of the heavy group 2 elements.

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Supporting Information Available: X-ray crystallographic files in CIF format for **I**, **II**, and **III**. This material is available free of charge via the Internet at http://pubs.acs.org.

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