1612 *Organometallics* **2008,** *27,* 1612–1616

s-Block Metal Complexes of the Bis(tetramethylcyclopentadienyl) Phosphonium Diylide $[Me(t\text{-}Bu)P(C_5Me_4)_2]^-$

Erik D. Brady,[†] Stephen C. Chmely,[†] Kumudini C. Jayaratne,[†] Timothy P. Hanusa,[*,†] and Victor G. Young, Jr.[‡]

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, and X-ray Crystallographic Laboratory, Chemistry Department, University of Minnesota, Minneapolis, Minnesota 55455

Received June 25, 2007

Treatment of the phosphonium salt $[Me(t\text{-}Bu)P(C_5Me_4H)_2]I$ with 2 equiv of KH produces the coordination polymer $\{K[Me(t\text{-}Bu)P(C_5Me_4)_2](thf)\}_\infty$. If the phosphonium salt reacts with a single equivalent of KH followed by $Ca[N(SiMe_3)_2]_2$, the calcium complex $[Me(t\text{-}Bu)P(C_5Me_4)_2]CaN(SiMe_3)_2$ is produced, which is structurally related to Cp'_2LnX organolanthanides. Density functional theory studies of the H_3E (E = C, Si, P)-substituted cyclopentadienyl ring indicate that the energy required for out-of-plane bending of the substituent decreases in the order $H_3C > H_3Si > H_3P$.

Introduction

Distinctive electronic, structural, and configurational properties can be incorporated into *ansa*-metallocenes, $[ACp'_2]MX_n$, by varying the identity of the *ansa*-bridge *A*.[1,2] Most commonly this is done while leaving the net charge of the $[ACp'_2]^n$ ligand at $n = -2$, as found not only in the catalytically important silyl bridged species $[R_2SiCp'_2]MX_2$,[3] but also in complexes with $A = R_2E$ (E = C, Ge, Sn) and RE′ (E′ = B, P^{III}, As^{III}).[2,4] In principle, *ansa* bridges with different charges could expand the range of complexes available from a given oxidation state of a metal, allowing the preparation of isostructural complexes from different metal families; e.g., $[R_2SiCp'_2]M^{III}X \approx [R_2PCp'_2]M^{II}X \approx Cp'_2M^{III}X$ (Figure 1).

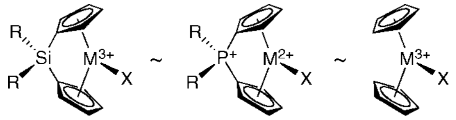


Figure 1. Isostructural silyl- and phosphonium-bridged metallocenes containing metals in different oxidation states. There is a formal similarity to unbridged bis(cyclopentadienyl) complexes (at right).

In the case of phosphonium-bridged complexes, Brintzinger has used the ligand $[Me_2P(2\text{-}Me\text{-}4\text{-}t\text{-}Bu\text{-}C_5H_2)_2]$ ($[Me_2PCp''_2]$) to prepare a series of Group 1 and 2 *ansa*-metallocenes.[5] Among these, the complex $Me_2PCp''BaN(SiMe_3)_2$ is formally similar to $Cp'_2LnN(SiMe_3)_2$ compounds, and even though the barium complex has not been structurally authenticated, it does not undergo Schlenk redistribution to $(Me_2PCp''_2)_2Ba$ and $Ba[N(SiMe_3)_2]_2$ in solution, as is common in heavy Group 2 cyclopentadienyl complexes.[6] Parkin has prepared the phosphonium bridged complexes $[\{Me_2P(C_5Me_4)_2\}MCl_2]^+I$ (M = Zr, Hf), and studied their reaction with methylating agents and CO.[7] These are compositionally related to the niobium(V) and tantalum(V) species $[(C_5H_5)_2MCl_2]^+X$ (M = Nb, X = I; M = Ta, X = Br, I), although reactions of the latter have not been extensively studied.[8]

In some cases, however, comparisons between phosphonium-bridged species and other complexes cannot be made at all. For example, calcium and barium both prefer to remain solvated with neutral oxygen donor ligands rather than bind to the phosphonium diylide $[Me_2P(fluorenyl)_2]$.[9] In contrast, although the metal–ligand coordination is sometimes considerably distorted, bis(fluorenyl) complexes such as $(fluorenyl)_2Ba(NH_3)_4$,[10] $(fluorenyl)_2BaL_n$ (L = thf, dme, pyridine),[11] and $[9\text{-}(Me_3Si)_3Si\text{-}fluorenyl)]M(thf)_2$ (M = Ca, Sr) can be isolated,[12] as can complexes with the silyl-bridged $[Me_2Si(fluorenyl)_2]^{2-}$ dianion.[13]

The kinetic stability offered by a chelating $[R_2PCp'_2]$ ligand is an attractive feature for complexes of highly electropositive metals, where ligand redistribution reactions are common. We

---

[*] Corresponding author. E-mail: t.hanusa@vanderbilt.edu.
[†] Vanderbilt University.
[‡] University of Minnesota.

(1) (a) Shapiro, P. J. *Coord. Chem. Rev.* **2002**, *231*, 67–81. (b) Erker, G. *Polyhedron* **2005**, *24*, 1289–1297. (c) Prashar, S.; Antinolo, A.; Otero, A. *Coord. Chem. Rev.* **2006**, *250*, 133–154. (d) Wang, B. *Coord. Chem. Rev.* **2006**, *250*, 242–258. (e) Voegele, J.; Dietrich, U.; Hackmann, M.; Rieger, B. *Metallocene-Based Polyolefins* **2000**, *1*, 485–512. (f) Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525–9546.

(2) Bourissou, D.; Freund, C.; Martin-Vaca, B.; Bouhadir, G. *Compt. Rend. Chim.* **2006**, *9*, 1120–1142.

(3) (a) Alonso-Moreno, C.; Antinolo, A.; Carrillo-Hermosilla, F.; Otero, A.; Rodriguez, A. M.; Sancho, J.; Volkis, V.; Eisen, M. *Eur. J. Inorg. Chem.* **2006**, 972–979. (b) Bryliakov, K. P.; Babushkin, D. E.; Talsi, E. P.; Voskoboynikov, A. Z.; Gritzo, H.; Schroeder, L.; Damrau, H.-R. H.; Wieser, U.; Schaper, F.; Brintzinger, H. H. *Organometallics* **2005**, *24*, 894–904. (c) Antinolo, A.; Fajardo, M.; Gomez-Ruiz, S.; Lopez-Solera, I.; Otero, A.; Prashar, S. *Organometallics* **2004**, *23*, 4062–4069. (d) Roesky, P. W.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 4705–4711.

(4) Shapiro, P. J. *Eur. J. Inorg. Chem.* **2001**, 321–326.

(5) Leyser, N.; Schmidt, K.; Brintzinger, H.-H. *Organometallics* **1998**, *17*, 2155–2161.

(6) Hanusa, T. P. *Organometallics* **2002**, *21*, 2559–2571.

(7) Shin, J. H.; Bridgewater, B. M.; Parkin, G. *Organometallics* **2000**, *19*, 5155–5159.

(8) Antinolo, A.; Fajardo, M.; Otero, A.; Royo, P. *J. Organomet. Chem.* **1984**, *265*, 35–43.

(9) Brady, E. D.; Hanusa, T. P.; Pink, M.; Young, V. G., Jr *Inorg. Chem.* **2000**, *39*, 6028–6037.

(10) Mösges, G.; Hampel, F.; Schleyer, P. v. R. *Organometallics* **1992**, *11*, 1769–1770.

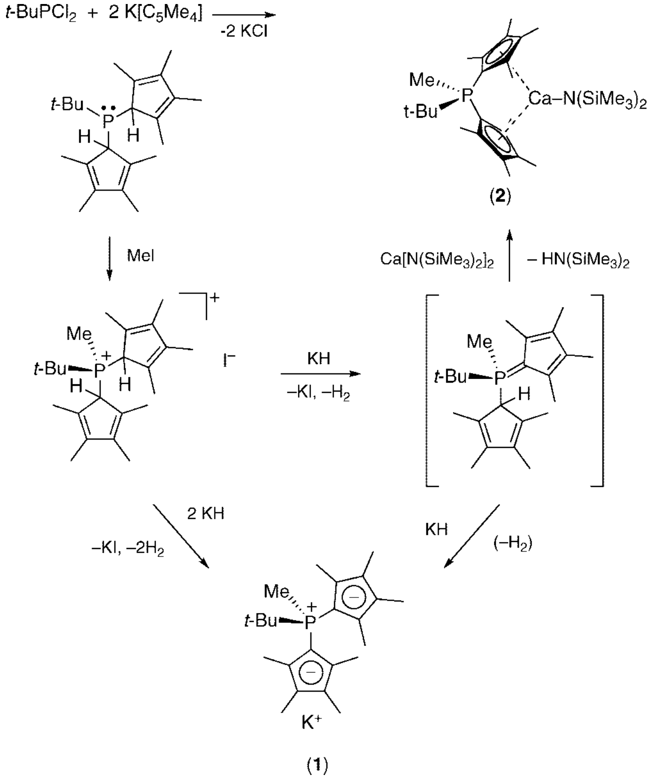
(11) Fichtel, K.; Hoexter, S.; Behrens, U. *Z. Anorg. Allg. Chem.* **2006**, *632*, 2003–2009.

(12) Feil, F.; Harder, S. *Eur. J. Inorg. Chem.* **2003**, 3401–3408.

(13) Harder, S.; Lutz, M.; Straub, A. W. G. *Organometallics* **1997**, *16*, 107–113.

10.1021/om700635c CCC: $40.75

Scheme 1. Summary of the Formation and Reactions of [Me(*t*-Bu)P(C_5Me_4H)$_2$]I



report here the synthesis and structural characterization of a phosphonium-bridged alkaline-earth complex that can be directly compared with trivalent lanthanide species, and a density functional theory study of bending in *ansa*-bridged cyclopentadienyl ligands.

Results and Discussion

Ligand Synthesis. The reaction of *t*-BuPCl$_2$ with 2 equiv of K[C_5Me_4H] in a mixture of THF/hexanes (5:1) at −80 °C produces the neutral phosphine (*t*-Bu)P(C_5Me_4H)$_2$ (Scheme 1). After the precipitated KCl is removed, treatment of the phosphine with MeI and stirring for 24 h precipitates the addition product [Me(*t*-Bu)P(C_5Me_4H)$_2$]I in moderate yield. When the phosphonium iodide is treated with 2 equiv of KH, the potassium salt of the diylide, K[Me(*t*-Bu)P(C_5Me_4)$_2$](thf) (**1**), is generated in 68% yield (Scheme 1). This general synthetic method has been used by others, and appears to be adaptable to a variety of alkyl groups and cyclopentadienyl-like ligands.[5,9]

Formation of Metal Complexes. The potassium salt **1** does not appear to react with CaI$_2$ in THF.[14] Several attempts were made to generate the neutral ylide Me(*t*-Bu)P(C_5Me_4H)(C_5Me_4), which should be convertible into metal complexes with the appropriate reagents. The reaction of [Me(*t*-Bu)P(C_5Me_4H)$_2$]I and 1 equiv of KN(SiMe$_3$)$_2$ in THF (to form the ylide in situ) followed by reaction with Ca[N(SiMe$_3$)$_2$]$_2$ lead only to the generation of **1**; the Ca[N(SiMe$_3$)$_2$]$_2$ remained unreacted.

In a similar manner, treatment of the phosphonium iodide with a single equivalent of KH in THF, followed by addition of Ca[N(SiMe$_3$)$_2$]$_2$ also formed some **1**. In this case, however, colorless crystals of the calcium complex [Me(*t*-Bu)P(C_5Me_4)$_2$]CaN(SiMe$_3$)$_2$ (**2**) were also isolated in low yield (Scheme 1). As 2 equiv of KN(SiMe$_3$)$_2$ or KH are required to form **1** from each equivalent of the phosphonium iodide, this suggests that once the ylide forms, it reacts more rapidly with a second equivalent of KN(SiMe$_3$)$_2$ or KH than does the phosphonium iodide, limiting the amount of free ylide available to react with Ca[N(SiMe$_3$)$_2$]$_2$. The partial diversion of the ylide to form **1**, combined with the high solubility of **2** (isolated by solvent evaporation), account for the reduced yield of the latter.

As was noted for the related Me$_2$PCp″BaN(SiMe$_3$)$_2$ complex,[5] **2** does not display Schlenk equilibrium in hydrocarbon solution. This is probably a consequence of its chelating rings, but could also be an indication that one of the expected products of Schlenk redistribution, [Me(*t*-Bu)P(C_5Me_4)$_2$]$_2$Ca, is too sterically bulky to form readily.[15]

Solid State Structures. K[Me(*t*-Bu)P(C_5Me_4)$_2$](thf). A crystal of K[Me(*t*-Bu)P(C_5Me_4)$_2$](thf) (**1**) was isolated from a saturated THF solution and used to determine its structure by X-ray diffraction. Each potassium atom has a coordinated thf molecule and is bound to a tetramethylcyclopentadiene ring on two phosphodiylide ligands, which produces a polymeric chain in the solid state. A diagram of the coordination polymer is given as Figure 2; selected bond lengths and angles are provided in Table S2 (Supporting Information).

An obvious point of comparison of **1** is with the polymeric structure of the phosphonium-bridged metallocene K[Me$_2$P(2-Me-4-*t*-Bu-C_5H_2]$_2$.[5] Both compounds were crystallized from THF, but the greater steric bulk of the *tert*-butyl substituent on the cyclopentadienyl ring of K[Me$_2$P(2-Me-4-*t*-Bu-C_5H_2]$_2$ may be the reason that it does not bind THF; each potassium is coordinated to three cyclopentadienyl rings instead. The differences in metal coordination produce other distinctive differences between the two structures. For example, the angle between the Cp′ planes in **1** is 147.7°, which is similar to the angles found in K[(*t*-BuNHSiMe$_2$)Cp](thf) (145.5°),[16] K[C_5Me_5](py)$_2$ (138°),[17] and K[Cp](OEt$_2$) (145°).[18] The interplanar Cp′ angles are nearly perpendicular (88.8°) in K[Me$_2$P(2-Me-4-*t*-Bu-C_5H_2]$_2$, however. The K atom is in a highly distorted environment in the latter complex, with a range of K−C contacts from 2.93 to 3.56 Å, and is at most η^3-coordinated to two rings of the *ansa*-ligand and η^5 to the adjacent ligand. In **1**, with the exception of one distance at 3.25 Å (K−C10′), the K−C contacts range from 2.95 to 3.14 Å, and are realistically described as η^5 to both rings. There is one close intrachain K−Me contact (K···C15) at 3.42 Å; this is near the sum of the ionic radius of 7-coordinate K$^+$ (1.46 Å[19]) and the van der Waals radius of a methyl group (2.0 Å[20]), and probably has only marginal energetic significance.

[Me(*t*-Bu)P(C_5Me_4)$_2$]CaN(SiMe$_3$)$_2$ (2). A crystal of **2** was isolated from a saturated hexanes solution. The calcium atom is bound to the [N(SiMe$_3$)$_2$] ligand and in an η^5-fashion to both tetramethylcyclopentadiene rings. One methyl group (C24) of the [N(SiMe$_3$)$_2$] group has close contacts with the calcium atom,

---

(14) The phosphonium iodide was also treated with *n*-BuLi in an effort to form a dilithio salt. Repeated attempts to obtain consistent elemental analysis on the resulting pale-yellow, air-sensitive solid (^{31}P NMR (THF-*d*$_8$): δ 13.3) were unsuccessful, and its exact composition is not known.

(15) A related compound is thought to form for [Me$_2$PCp″]$_2$Ba (ref 5), but in this case the metal center is larger (Ba^{2+} vs Ca^{2+}), with a correspondingly larger coordination sphere.

(16) Schaeffer, W. P.; Cotter, W. D.; Bercaw, J. E. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1993**, *C49*, 1489–1492.

(17) Rabe, G.; Roesky, H. W.; Stalke, D.; Pauer, F.; Sheldrick, G. M. *J. Organomet. Chem.* **1991**, *403*, 11–19.

(18) Jordan, V.; Behrens, U.; Olbrich, F.; Weiss, E. *J. Organomet. Chem.* **1996**, *517*, 81–88.

(19) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *32*, 751–767.

(20) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

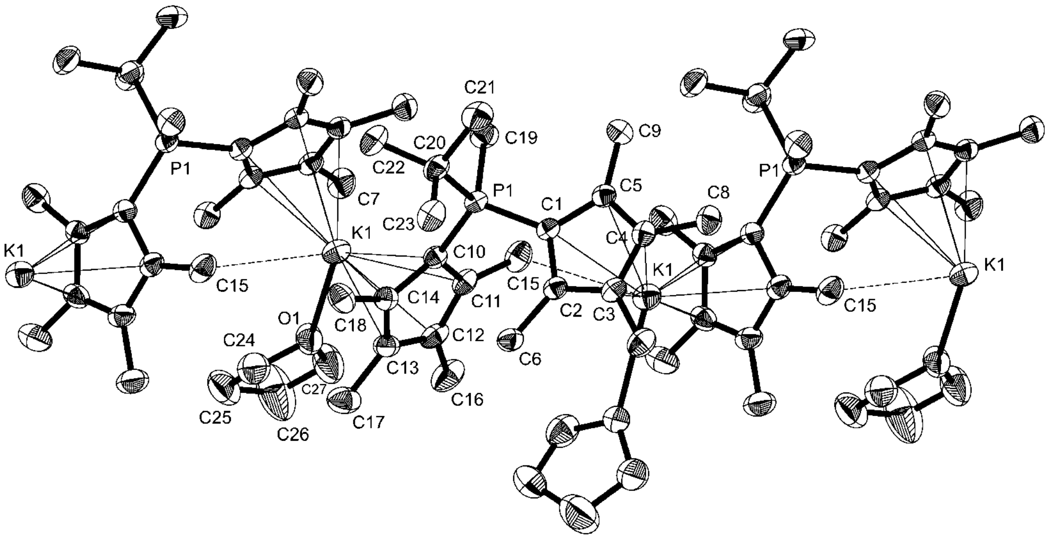


Figure 2. Diagram of the polymeric {K[Me(*t*-Bu)P(C_5Me_4)$_2$]}(thf)$_\infty$ structure. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms have been omitted for clarity.

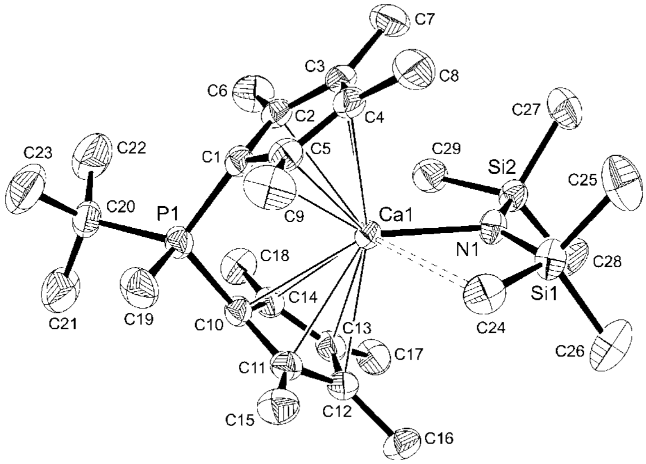


Figure 3. Diagram of the non-hydrogen atoms of [Me(*t*-Bu)P(C_5Me_4)$_2$]CaN($SiMe_3$)$_2$ (**2**). Thermal ellipsoids are shown at the 50% probability level.

suggestive of an agostic interaction. A diagram of the molecule is provided as Figure 3, displaying the numbering scheme referred to in the text. Selected bond lengths and angles are provided in Table 3.

The average calcium–carbon (ring) distances in **2** (2.78 and 2.76 Å) are somewhat longer than the 2.68 or 2.72 Å average distances found in [C_5H_3-1,3-($SiMe_3$)$_2$]Ca(thf)[21] or (C_5Me_4*i*-Pr)$_2$(1,3-(*i*-Pr)$_2$-4,5-Me_2-imidazol-2-ylidene)Ca,[22] respectively, despite the formally 7-coordinate Ca^{2+} centers in all three complexes. Part of the Ca–C bond lengthening in **2** is a result of the ring chelation introduced by the phosphorus bridge, which prevents the cyclopentadienyl rings from adopting their preferred distances. This is reflected in the range in bond distances (2.682(2)–2.873(2) Å; $\Delta_{Ca-C} = 0.19$ Å), which is notably larger than is typical in nonbridged calcium metallocenes (cf. $\Delta_{Ca-C} = 0.07$ Å in (C_5Me_5)$_2$Ca[23] and 0.06 Å in [C_5H_3-1,3-($SiMe_3$)$_2$]Ca(thf),[21] although note $\Delta_{Ca-C} = 0.15$ Å in [C_5(*t*-Bu)H_4]$_2$Ca(thf)$_2$[6]). The average bending angle at the *ipso*-ring carbons (e.g., P(1)–C(6,20)–ring centroid) is 19.8°, 6° larger than the average bending observed in the related [Me_2P(2-Me-4-*t*-Bu-C_5H_2)$_2$Ba(thf)$_3$]$^+$ cation.[5]

The Ca–N bond length (2.293(2) Å) in **2** is identical within error to the 2.29(1) and 2.30(1) Å Ca–N distances found in the two independent molecules of Cp^{4i}Ca[N($SiMe_3$)$_2$](thf) (Cp^{4i} = C_5(i-Pr)$_4$H);[24] it is also similar to analogous bonds found in dimeric {Ca[N($SiMe_3$)$_2$]$_2$}$_2$ (2.282(6) and 2.267(7) Å)[25] and monomeric Ca[N($SiMe_3$)$_2$]$_2$(dme) (2.271(3) Å).[25]

The relatively open coordination sphere in **2** permits the existence of an agostic interaction[26] between the calcium center and one of the methyl groups on the amido ligand. At 3.03 Å, the Ca···C24 contact is comparable to that observed in Cp^{4i}Ca[N($SiMe_3$)$_2$](thf) (2.95 Å).[24] The differences between the Ca···Si contacts (3.27 and 3.45 Å) are also consistent with an agostic interaction, and a similar difference is observed in Cp^{4i}Ca[N($SiMe_3$)$_2$](thf) (at 3.20 and 3.60 Å).[24] The near-zero (1.1°) torsion angle for Ca–N–Si1–C24 reflects the alignment of the trimethylsilyl group with the calcium.

It is instructive to compare the structure of **2** with those of (C_5Me_5)$_2$SmN($SiMe_3$)$_2$[27] and (C_5Me_5)$_2$YN($SiMe_3$)$_2$,[28] which have the common trivalent organolanthanide structural motif, Cp′$_2$LnX. Seven-coordinate Ca^{2+} and Sm^{3+} both possess radii that are slightly larger than 1.0 Å (1.06 Å for Ca, 1.02 Å for Sm),[19] and both the average metal–carbon distances (2.77 Å for Ca, 2.75 Å for Sm) and the metal–nitrogen distances in **2** and the samarium complex are similar (2.29 Å for Ca, 2.30 Å for Sm).[27] There are no close Sm–C contacts in (C_5Me_5)$_2$-SmN($SiMe_3$)$_2$ that suggest an agostic interaction, and the Sm–N–Si angles are equivalent (115.0° and 116.5°).[27]The yttrium compound, in contrast, does display an agostic interaction between yttrium and a carbon atom (2.970(6) Å) on the amido ligand. The smaller radius of 7-coordinate Y^{3+} (0.96 Å[19])

---

[21] Engelhardt, L. M.; Junk, P. C.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1988**, 1500–1501.

[22] Schumann, H.; Gottfriedsen, J.; Glanz, M.; Dechert, S.; Demtschuk, J. *J. Organomet. Chem.* **2001**, *617*, 588–600.

[23] Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *Organometallics* **1990**, *9*, 1128–1134.

[24] Burkey, D. J.; Alexander, E. K.; Hanusa, T. P. *Organometallics* **1994**, *13*, 2773–2786.

[25] Westerhausen, M.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1991**, *604*, 127–140.

[26] Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395–408.

[27] Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1993**, *12*, 2618–2633.

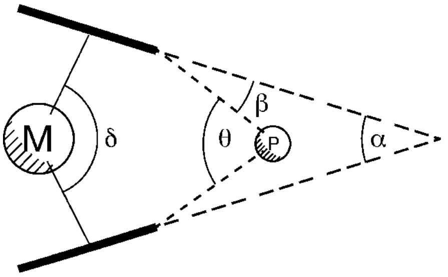


Figure 4. Geometric parameters in a phosphonium-bridged *ansa* metallocene. The angles are as follows: α = angle between the ring planes (ring tilt); β = tilt of the Cp ring relative to the $P-C_{ipso}$ bond (ideally, $\beta = (\theta - \alpha)/2$); δ = ring centroid−M−ring centroid angle; θ = angle at phosphorus.

is reflected in a slightly shorter M−N bond distance (2.274(5) Å) than is found in the calcium or samarium analogues.

Computational Results. C- and especially Si-bridged *ansa* metallocenes have been the subject of repeated computational investigations;[13,29] their phosphonium-bridged counterparts, in contrast, have received much less attention. The P−C distance (1.746 Å) and the C−P−C′ angle (115.9°) calculated with DFT methods (B3PW91/6-31+G(d)) for the free $[Me_2P(C_5H_4)_2]$ anion[9] were not greatly different from those of the substituted, complexed $[Me_2P(2\text{-}Me\text{-}4\text{-}(t\text{-}Bu)\text{-}C_5H_2)_2]$ anion,[5] although the C−P−C′ angles in the two complexes (112.8(4)° in the K complex; 109.5(2)° in the barium compound) close somewhat to accommodate the metals. Recalculated values for $[Me_2P(C_5H_4)_2]$ with the slightly larger basis set 6-31+G(d,p), along with the alkylated derivatives $[Me_2P(C_5Me_4)_2]^-$ and $[Me_2P(C_5Me(t\text{-}Bu)H_3)_2]$, and the $[Me_2P\text{-}(fluorenylidene)_2]$ anion are reported in Table S4 (Supporting Information). Little change in the P−C distance or the C−P−C′ angle occurs on alkylation or on substitution of the fluorenyl moiety for the cyclopentadienyl ring.

The distortions in bond angles that accompany the coordination of *ansa*-bridged ligands to metals are well-known.[2,7] These can be categorized by reference to various angles (see Figure 4), and have been tabulated for structurally authenticated phosphonium-bridged species in Table S5 (Supporting Information). The angles at phosphorus (θ) are close to the tetrahedral ideal in the two alkaline-earth complexes, whereas the smaller metal centers of the transition metal compounds display roughly 10° of compression. The tilting of the Cp ring relative to the $P-C_{ipso}$ bond (β) varies from a low of 13° in $[Me_2P(2\text{-}Me\text{-}4\text{-}t\text{-}Bu\text{-}C_5H_2)_2Ba(thf)_3]BPh_4$ to almost 38° in the highly distorted $[\{Me(Ph)P(C_5H_4)_2\}Fe]^+$ cation. Harder has shown with the aid of Hartree–Fock calculations that the energy required to bend a silyl group on the Cp anion is approximately half that required for an alkyl group,[13] a consequence of diminished delocalization in the Cp ring. We were interested in determining the extent that this might be true for phosphonium substituents.

DFT methods were used to complete a set of calculations similar to those performed by Harder. They confirm that compared to the alkylated $[H_3CCp]$ anion, the *ipso* carbon of the $[H_3SiCp]$ anion bears the most negative charge; this is also true for the phosphonium ligand (Figure 5). Progressive loss of delocalization is evident in the change from carbon to silicon to phosphorus, as revealed in the lengthening of $C_{ipso}-C_\alpha$ and $C_\beta-C_\beta'$ bonds relative to the $C_\alpha-C_\beta$ bonds. This can be quantified in the ratio $\Delta_L = {}^1/_2(C_{ipso}-C_\alpha + C_\beta-C_\beta')/(C_\alpha-C_\beta)$, which equals 0.998, 1.013, and 1.034 for C, Si, and P, respectively. Bending the H_3E substituent out of the plane increases the charge on the C_{ipso} atom by 35% in the case of E = C (HF calculations put the change at 60%),[13] but leaves the charge unchanged when E = Si, and decreases the charge slightly (13%) in the phosphonium ligand. The delocalization decreases further on bending, but the change in Δ_L for a 50° bend is greatest for C (3.0%); that for Si (0.9%) and P (0.6%) is small.

The relative energetics of bending hold over a wide range of angles. The bending of a silyl group is always less costly than that of an alkyl, often by more than a factor of 2 (Figure 6). For a β angle of 30°, for example, the energetic cost of alkyl to silyl group bending is 3.5:1. The phosphonium ligand is even easier to bend, with an alkyl to phosphonium ratio of 8.7:1. Part of the reason for this is the previously mentioned loss of delocalization in the cyclopentadienyl rings in the Si- and P-based systems even prior to bending. In addition, the neutrality of the phosphonium-substituted ring also makes the ring easier to bend, as less redistribution of charge is necessary.

Conclusion

Phosphonium-bridged *ansa*-metallocenes, although not yet widely encountered in organometallic chemistry, display many of the features of their silyl-bridged counterparts, including a high degree of flexibility in bending at the C_{ipso} of the cyclopentadienyl ring. In the context of Group 2 metal chemistry, the $[R_2PCp'_2]^-$ anion offers a uninegative charge with the coordination environment of two cyclopentadienyl rings, opening possibilities for a range of Schlenk redistribution-resistant $[R_2PCp'_2]MX$ complexes, with intriguing parallels to organolanthanide species. We are exploring such analogies further.

Experimental Procedures

General Considerations. All manipulations were performed with the rigorous exclusion of air and moisture with use of high-vacuum, Schlenk, or glovebox techniques. Proton, carbon ($^{13}C\{^1H\}$), and phosphorus ($^{31}P\{^1H\}$) NMR spectra were obtained at 25 °C on a Bruker DPX-300 spectrometer at 300, 75.5, and 121.4 MHz, respectively, and were referenced to the residual proton or ^{13}C resonances of THF-d_8 (δ 3.58 (^1H), 67.4 (^{13}C)), C_6D_6 (δ 7.15 (^1H)), CD_2Cl_2 or for ^{31}P NMR, an external standard of H_3PO_4. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Melting points were determined in sealed capillaries.

Materials. Anhydrous calcium iodide was a commercial sample (Cerac, 95%) and was heated under vacuum (150 °C, 10^{-4} Torr) to ensure complete removal of water and residual amounts of free iodine. $Ca[N(SiMe_3)_2]_2$ was prepared as described previously.[9] Potassium hydride was purchased from Strem and washed with hexanes in a glovebox prior to use. $C_5Me_4H_2$, $K[N(SiMe_3)_2]$, $t\text{-}BuPCl_2$, CD_2Cl_2, and MeI were purchased from Strem, Acros, or Aldrich and used as received. $K[C_5Me_4H]$ was made by the reaction of $C_5Me_4H_2$ with $K[N(SiMe_3)_2]$. THF, toluene, and hexanes were distilled under nitrogen from potassium benzophenone ketyl.[30] C_6D_6 and THF-d_8 were vacuum distilled from Na/K (22/78) alloy and stored over type 4A molecular sieves prior to use.

Synthesis of $[Me(t\text{-}Bu)P(C_5Me_4H)_2]I$. $t\text{-}BuPCl_2$ (3.13 g, 19.7 mmol) was dissolved in hexanes (40 mL) in a 100 mL Schlenk flask. $K[C_5Me_4H]$ (6.43 g, 40.1 mmol) was placed in a 500 mL

---

(28) den Haan, K. H.; de Boar, J. L.; Teuben, J. L.; Spek, A. L.; Kojić-Prodić, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726–1733.

(29) (a) Janak, K. E.; Shin, J. H.; Parkin, G. *J. Am. Chem. Soc.* **2004**, *126*, 13054–13070. (b) Kirillov, E.; Toupet, L.; Lehmann, C. W.; Razavi, A.; Kahlal, S.; Saillard, J.-Y.; Carpentier, J.-F. *Organometallics* **2003**, *22*, 4038–4046. (c) Dunn, A. R.; Sweet, L. E.; Wiser, D. C.; LoCoco, M. D.; Jordan, R. F. *Organometallics* **2004**, *23*, 5671–5680. (d) Talarico, G.; Blok, A. N. J.; Woo, T. K.; Cavallo, L. *Organometallics* **2002**, *21*, 4939–4949.

(30) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, UK, 1988.

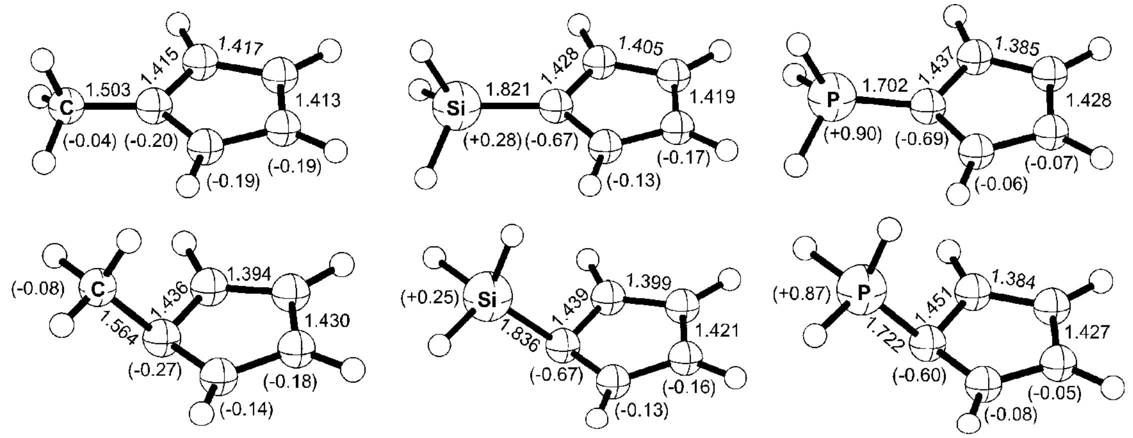


Figure 5. Geometries (B3PW91/6-31+G(d,p); C_s symmetry) and group charges (NPA, in parentheses) for undistorted and bent ($\beta = 50°$) [H_3CCp], [H_3SiCp], and [H_3PCp] rings (left to right, respectively).

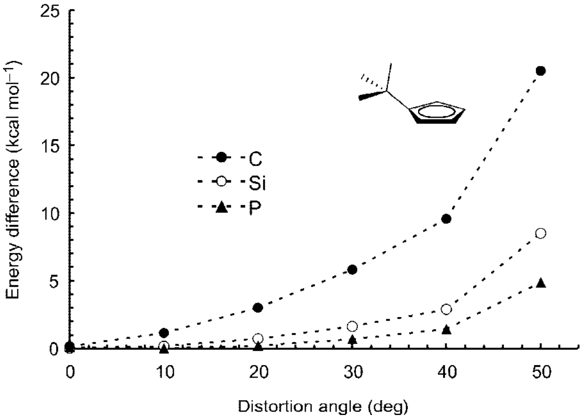


Figure 6. Relative energies (B3PW91/6-31+G(d,p)) as a function of bending the H_3E substituent out of the Cp ring plane for [H_3CCp], [H_3SiCp], and [H_3PCp] rings.

Schlenk flask and slurried in 200 mL of THF. At −80 °C, the dichlorophosphine solution was slowly cannulated into the constantly stirred K[C_5Me_4H] solution. The mixture immediately turned yellow and the cold bath was removed. The reaction was stirred for 4 h, after which the solvent was removed under vacuum to yield an orange waxy solid. The solid was extracted with hexanes (50 mL), and the extract was filtered over a Schlenk frit to remove precipitated KCl. The light orange hexanes filtrate was treated with MeI (1.40 mL, 22.5 mmol) and the resulting mixture was stirred. The following day, a white precipitate had formed, which was separated by filtration over a medium porosity glass frit and washed with small amounts of hexanes (2 × 10 mL). [Me(*t*-Bu)P(C_5Me_4H)$_2$]I (4.36 g) was collected in 46% yield (based on MeI), mp 98 °C dec. Anal. Calcd for $C_{23}H_{38}IP$: C, 58.48; H, 8.11; P, 6.56. Found: C, 58.74; H, 8.42; P, 6.34. The NMR spectra indicate the existence of several isomers; the resonances of the major one are (^1H, CD_2Cl_2) δ 4.13 (d, C_5Me_4H, $J_{P-H} = 20$ Hz), 2.03 (d, C_5Me_4H, $J_{P-H} = 6.8$ Hz), 1.85 (d, P−*Me*, $J_{P-H} = 6.8$ Hz), 1.52 (d, C_5Me_4H, $J_{P-H} = 8.9$ Hz), 1.46 (d, C_5Me_4H, $J_{P-H} = 8.3$ Hz), 1.33 (singlet, P-C*Me*$_3$). ^{31}P NMR (CD_2Cl_2) δ 32.2.

Synthesis of K[Me(*t*-Bu)P(C_5Me_4)$_2$](thf) (1). [Me(*t*-Bu)P-(C_5Me_4H)$_2$]I (0.450 g, 0.952 mmol) was dissolved in THF (30 mL). KH (0.076 g, 1.90 mmol) was added to the pale yellow solution and the mixture was stirred. The following day, the turbid solution was filtered to yield an orange solution. The solvent was removed under vacuum and hexanes (5 mL) was added to wash the residual solid. The resulting slurry was filtered over a medium porosity frit. The solid was thoroughly dried to afford 0.295 g (68%) of K[Me(*t*-Bu)P(C_5Me_4)$_2$](thf) (**1**) as an orange, air-sensitive solid, mp 241 °C. Anal. Calcd for $C_{27}H_{44}KOP$: C, 71.32; H, 9.75; P, 6.81. Found: C, 74.00; H, 9.82; P, 6.51. The high carbon value may reflect partial loss of coordinated THF. ^1H NMR (THF-d_8) δ 3.54 (s, 4H, α-C_4H_8O), 2.03 (s, 12H, C_5Me_4), 1.87 (s, 12H, C_5Me_4), 1.69 (s, 4H, β-C_4H_8O), 1.28 (s, 9H, P−C*Me*$_3$), 1.21 (d, 3H, P−*Me*, $J_{P-H} = 11.6$ Hz). ^{13}C NMR (THF-d_8) δ 116.0 (C_5Me_4), 115.8 (C_5Me_4), 115.7 (C_5Me_4), 115.5 (C_5Me_4), 86.4 (P−C_5Me_4), 85.1 (P−C_5Me_4), 66.8 (α-C_4H_8O), 36.4 (P−C*Me*$_3$), 35.7 (C_5Me_4), 27.3 (P−*C*Me$_3$), 26.4 (β-C_4H_8O), 15.4 (C_5Me_4), 12.0 (P−*Me*). ^{31}P NMR (THF-d_8) δ 15.3.

Synthesis of [Me(*t*-Bu)P(C_5Me_4)$_2$]CaN($SiMe_3$)$_2$ (2). [Me(*t*-Bu)P(C_5Me_4H)$_2$]I (0.300 g, 0.635 mmol) was dissolved in THF (50 mL). KH (0.025 g, 0.62 mmol) was added and the resulting mixture was stirred for 3 h. The cloudy solution was filtered through a pipet packed with glass wool and Celite 521. Ca[N($SiMe_3$)$_2$]$_2$ (0.228 g, 0.635 mmol) was added and the solution was stirred. The following day, a small amount of precipitate was observed that was removed by filtration through a pipet packed with glass wool and Celite 521. The filtrate was placed under vacuum to afford an oily orange solid. Hexanes (2 mL) was added and the mixture was subsequently filtered through a medium porosity glass frit. The filtrate was collected in a vial and allowed to evaporate slowly. Additional THF (4 mL) was added to the solid that was retained on the frit and the solution filtered as before. Small cubes formed from the THF filtrate; these contained **1**, identified with ^1H and ^{31}P NMR spectra. Large colorless X-ray quality crystals formed on evaporation of the hexanes filtrate. These crystals were identified as [Me(*t*-Bu)P(C_5Me_4)$_2$]CaN($SiMe_3$)$_2$ (**2**) (0.036 g, 11% yield), mp 222–226 °C dec. Anal. Calcd for $C_{29}H_{54}CaNPSi_2$: C, 64.03; H, 10.01. Found: C, 64.52; H, 10.24. ^1H NMR (C_6D_6) δ 2.16 (br s, 12H, C_5Me_4), 2.08 (s, 12H, C_5Me_4), 1.83 (d, 3H, P−*Me*, $J_{P-H} = 12.1$ Hz), 1.13 (d, 9H, P−C*Me*$_3$, $J_{P-H} = 16.0$ Hz), 0.23 (s, 18H, Si*Me*$_3$). ^{13}C NMR (THF-d_8) δ 116.0 (C_5Me_4), 115.9 (C_5Me_4), 115.6 (C_5Me_4), 115.4 (C_5Me_4), 86.2 (P−C_5Me_4), 85.2 (P−C_5Me_4), 37.5 (P−C*Me*$_3$), 37.1 (C_5Me_4), 27.4 (d, P−*C*Me$_3$, $J_{P-C} = 12$ Hz), 15.6 (C_5Me_4), 12.2 (d, P−*Me*, $J_{P-C} = 4$ Hz), 1.47 (Si*Me*$_3$). ^{31}P NMR (C_6D_6) δ 25.0.

Acknowledgment. We thank the National Science Foundation for support of this research. EDB was supported with a GAANN Fellowship from the Department of Education.

Supporting Information Available: Crystallographic data, tables of geometric parameters, files in CIF format for **1** and **2**, and computational details for phosphonium Cp′ species. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700635C