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The Phosphonium Dibenzylide Anion as a Ligand in Organobarium Chemistry

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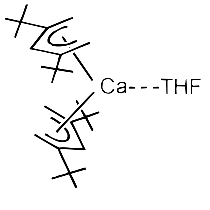
The structural analysis of $[Ph_2P(4\text{-methylbenzylide})_2]_2Ba$ represents that of the first organobarium compound not belonging to the cyclopentadienyl series. The structure consists of two C_2-symmetric phosphonium ligands (of opposite chirality) encapsulating the Ba^{2+} ion. The Ba^{2+} ion is in bonding contact with the ylidic and benzylic ring carbon atoms. The benzylidic carbon adopts a planar sp^2 bonding geometry, in the solid state as well as in solution. In solution, a dynamic process exchanges the two antipodes of the chiral dibenzylide ligands. *Ab initio* calculations and NPA charge analyses show that the di-ylide ligands in $[Ph_2P(4\text{-methylbenzylide})_2]_2Ba$ should be described as species with highly polar $P^+{-}C^-$ bonds. Calculations and detailed analysis of the benzyl ring geometries in the crystal structure show that the negative charge on the benzyl group is mainly localized on the ylidic carbon. The bonding geometries at P are distorted from tetrahedral geometry such as to increase the effect of C(lone pair) $\rightarrow \pi^*$ (PR_2) hyperconjugation. Thus, ylene character in the P−C bonds of dibenzylide anions is not negligible.

Introduction

Over the last decade, syntheses and structural investigations of well-defined organometallic compounds of the heavier alkaline-earth metals (Ca, Sr, Ba) have attracted much interest.[1] This is partly due to the use of heavier alkaline-earth metals in chemical vapor deposition (CVD).[1,2] Syntheses and structure elucidations, however, have mainly focused on volatile metal alkoxides[2] and (substituted) cyclopentadienides.[1b−d,3] Structural investigations on the more reactive (stronger nucleophilic) organoalkaline-earth complexes are scarce. Up to now, only four non-Cp organometallic complexes of the heavier alkaline-earth metals have been structurally characterized: an “open” calcocene[4] (**1**), butadienyl complexes of Ca and Sr (**2a,b**),[5] and an organocalcium complex with the sterically demanding carbanion $(TMS)_2HC^-$ (**3**).[6] The necessity to isolate and structurally investigate well-defined non-Cp organometallic complexes of the heavier alkaline-earth metals (especially of Ba) is therefore obvious.



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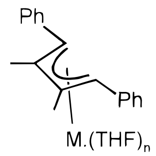
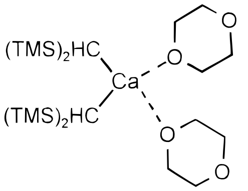


2a M = Ca, n = 3
2b M = Sr, n = 4



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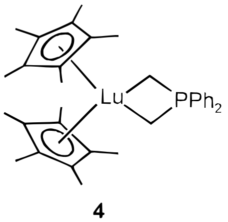
As has been indicated earlier,[1b,c] the main problem in organobarium chemistry is the low electronegativity and large size of the Ba^{2+} ion. This makes organobarium species more ionic and consequently more reactive than their Mg analogues. Additionally, the large metal radius puts high demands on the saturation of its coordination sphere, a prerequisite for obtaining well-defined soluble polar organometallic complexes. In this respect, the comparison with organolanthanide chemistry has been made[1b] and the use of large groups to control metal nuclearity and block decomposition routes was shown to be of similar utility in the cyclopentadienyl chemistry of barium. Since the phosphonium bis-ylidic anion ($R'_2P^+R^-{}_2$, a bidentate but monoanionic ligand) has shown its potential in the syntheses of well-defined highly reactive complexes of the rare-earth metals (*e.g.* **4**[7] and **5**[8]), we now direct our



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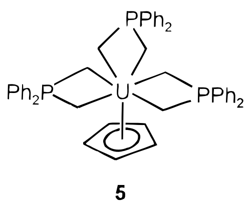

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[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1996.

[1] For reviews see: (a) Lindsell, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 1, Chapters 2−4. (b) Hanusa, T. P. *Polyhedron* **1990**, *9*, 1345. (c) Hanusa, T. P. *Chem. Rev.* **1993**, *93*, 1023. (d) Burkey, D. J.; Hanusa, T. P. *Comments Inorg. Chem.* **1995**, *17*, 41.

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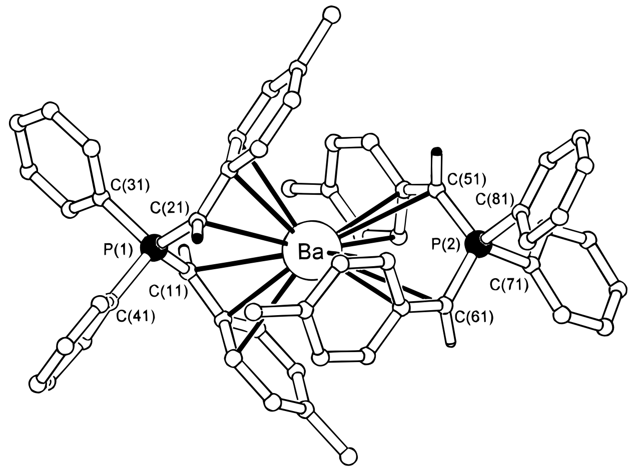
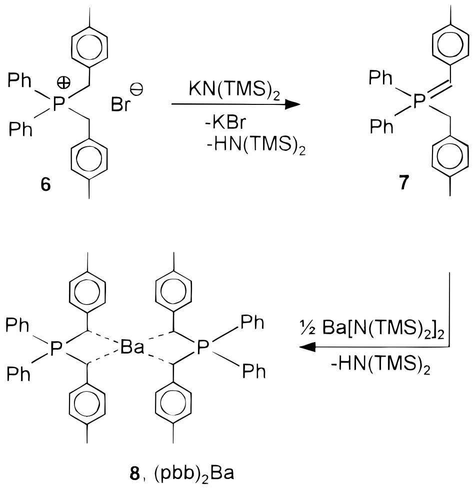


Figure 1. Crystal structure of (pbb)$_2$Ba (**8**). Hydrogen atoms have been partially omitted for clarity. Systematic numbering scheme: for C(*xy*), *x* gives the group number and *y* the atom within the group (see also Figure 2).

Scheme 1



attention to the preparation and structural investigation of barium compounds of this type. The molecular and electronic structure of phosphonium bis-ylide anions is discussed with the help of a series of *ab initio* calculations.

Results and Discussion

A phosphonium dibenzylide anion seems an ideal ligand to fill the large coordination sphere of barium. The bis(phosphonium dibenzylide)barium complex **8** ((pbb)$_2$Ba in short) can be obtained in high yield as an orange crystalline product (Scheme 1).

The crystal structure of (pbb)$_2$Ba (Figure 1) shows a monomeric organobarium compound in which the Ba atom is fully shielded by two monoanionic bidentate pbb ligands. Although the (pbb)$_2$Ba monomer has no crystallographic symmetry, the pbb ligands are approximately C_2 symmetric and thus chiral. The coordination sphere of the Ba^{2+} ion is formed by two C_2-symmetric ppb anions of opposite chirality, which fit into each other. Therefore, the (pbb)$_2$Ba molecule itself adopts approximate S_4 symmetry and is achiral.

Table 1. Selected Atom Distances (Å) and Angles (deg) for (pbb)$_2$Ba[a]

	$x = 1$	$x = 2$	$x = 3$	$x = 4$
Ba−C(*x*1)	3.217(7)	3.106(7)	3.299(8)	3.454(6)
Ba−C(*x*2)	2.981(6)	3.031(6)	3.014(6)	3.003(6)
Ba−C(*x*3)	3.159(6)	3.193(7)	3.155(7)	3.074(7)
Ba−C(*x*4)	3.722(7)	3.944(7)	3.669(8)	3.435(7)
Ba−C(*x*5)	4.069(7)	4.479(8)	4.051(7)	3.711(7)
Ba−C(*x*6)	3.894(7)	4.333(8)	3.895(6)	3.665(7)
Ba−C(*x*7)	3.391(7)	3.661(7)	3.438(6)	3.322(7)

P(1)−C(11)	1.727(7)	P(2)−C(51)	1.724(7)
P(1)−C(21)	1.721(8)	P(2)−C(61)	1.721(7)
P(1)−C(31)	1.823(7)	P(2)−C(71)	1.821(8)
P(1)−C(41)	1.831(6)	P(2)−C(81)	1.819(7)
P(1)···Ba	3.714(6)	P(2)···Ba	3.944(6)

C(11)−P(1)−C(21)	115.9(3)	C(51)−P(2)−C(81)	103.9(3)
C(31)−P(1)−C(41)	102.9(3)	C(61)−P(2)−C(71)	106.2(4)
C(11)−P(1)−C(31)	103.8(4)	C(61)−P(2)−C(81)	113.5(4)
C(11)−P(1)−C(21)	113.5(3)	C(11)−Ba−C(21)	71.7(2)
C(21)−P(1)−C(31)	114.2(4)	C(11)−Ba−C(51)	146.5(2)
C(21)−P(1)−C(41)	106.0(3)	C(11)−Ba−C(61)	147.6(2)
C(51)−P(2)−C(61)	116.7(4)	C(51)−Ba−C(61)	60.1(2)
C(71)−P(2)−C(81)	103.1(3)	P(1)···Ba···P(2)	173.5(2)
C(51)−P(2)−C(71)	112.7(4)		

[a] See Figures 1 and 2 for the numbering scheme.

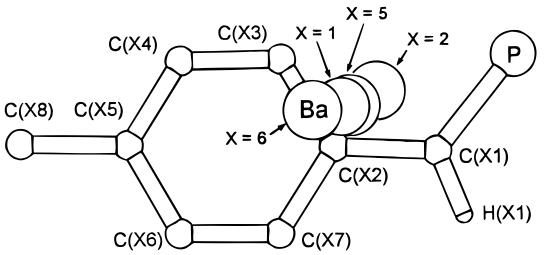


Figure 2. 2. Projections perpendicular to the benzylide plane, showing the four different geometries of Ba−benzylide coordination encountered in (pbb)$_2$Ba (the four different benzyl groups are fitted on each other). Systematic numbering scheme: for C(*xy*), *x* gives the benzylide group number and *y* the number of the atom in the group.

Projections of the Ba atom on the four crystallographically inequivalent benzyl planes show the different benzyl−Ba bonding geometries (Figure 2). Although there is some variation in benzyl−Ba bonding, the benzyl groups coordinate on average in an exocyclic η^3-like fashion typical for polar benzylmetal compounds.[9] The Ba−benzyl bonding should be considered as a highly electrostatic interaction.[1,10] Thus, the energy of the interaction between Ba^{2+} and the various benzyl C atoms can be estimated to be inversely proportional with the Ba−C distance and also related to the electron distribution in the benzylic π-system. It is therefore arbitrary to pose a borderline value for the discrimination between bonding and nonbonding or weakly Ba−C interactions. Projections in Figure 2 and an estimation of the distribution of negative charge (*vide infra*) show that Ba−C bonds to the benzylic carbon and one of the ortho ring carbons are dominant.

The determination (and refinement) of the benzylide hydrogen positions allows a reliable assignment of the hybridization state of the ylidic carbon. For all four ylidic carbons, the angles with their C, H, and P bonding partners add within error to 360°, illustrating perfectly planar sp^2-bonding geometries.

Currently, no other structures of heavier alkaline-earth bis-ylides have been reported. There is, however,

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[9] Setzer, W.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

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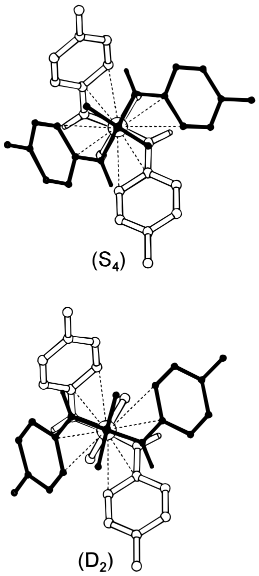
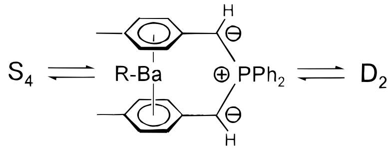


Figure 3. 3. Changes in the chirality of one of the pbb ligands in the S_4-symmetric structure of $(pbb)_2Ba$, resulting in a D_2-symmetric complex with similar molecular packing and pbb−Ba bonding.

a structure of a closely related alkali-metal complex $Me_2P(benzylide)_2^-$ K^+, which forms a polymer in the solid state.[11] In this structure, the dibenzylide anion adopts a comparable C_2 symmetry and the K^+ ion, which is about equal in size to the Ba^{2+} ion, is similarly bonded between the two benzyl systems.

Crystals of $(pbb)_2Ba$ dissolve well in benzene, toluene, and THF. A gated-decoupled ^{13}C NMR spectrum of $(pbb)_2Ba$ in toluene shows for the benzylide carbon a $^1J(C,H)$ value of 156.0 Hz. This indicates an averaged planar sp^2 bonding geometry[12] at the benzylide carbon and is consistent with the solid-state structure. However, the ^1H NMR spectrum (at +20 °C) shows very broad singlets for the benzyl ring protons. Heating to +45 °C is sufficient to obtain an AB pattern. This behavior is inconsistent with the rigid solid-state structure, in which two different ortho and two different meta hydrogens (anti or syn to P) occur. The equivalence of the different ortho and meta protons suggests a fluxional process in which the aromatic rings (not the ylidic carbon) loose their bond with Ba, rotate around the $C_{ipso}-C_{para}$ axis, and bind to Ba again. Cooling to −30 °C freezes this fluxional process, and as expected, several broad (partly overlapping) signals for the ortho and meta hydrogens appear. However, cooling also results in a broadening and decoalescence (T_{coal} = −20 °C, $\Delta\nu$ = 44 Hz) of the signal for the *p*-Me group of the benzylide ligand. This means that the suggested fluxional process is more than simply a rotation of the benzylide rings, since this would leave Me groups equivalent. Likely, the C_2-symmetric chiral pbb ligands are, at room temperature, in fast exchange with their chiral antipodes. Switching the chirality of one of the pbb ligands in the S_4-symmetric solid-state structure of $(pbb)_2Ba$ results in a change from S_4 to D_2 symmetry. Models, depicted in Figure 3, show that such a change hardly affects the molecular packing and coordination geometry at Ba. These models account for the observed exchange of the benzylide ring hydrogens (anti ↔ syn with respect to P) and explains the appearance of two Me resonances at low temperature. Line broadening but no coalescence can be observed for the ylidic hydrogen and the phenyl hydrogens, implying that their environment is hardly different in the D_2 and S_4 diastereomers. The conversion of S_4-$(pbb)_2Ba$ into D_2-$(pbb)_2Ba$ may proceed via a transition state in which the Ba−ylide bond is broken and only the aromatic rings coordinate on Ba (**9**; $\Delta G^\ddagger$ estimated from NMR is 12.4 kcal/mol).



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A ^1H NMR spectrum of $(pbb)_2Ba$ dissolved in THF shows a sharp AB pattern for the benzylide ring protons already at room temperature. This indicates that exchange processes in this solvent are much faster, likely because THF is able to stabilize the transition state for exchange by additional solvation of the Ba^{2+} ion.

The relationship between the molecular and electronic structure of di-ylide anions is discussed here with the aid of *ab initio* calculations (Figure 4). Possible ylene−ylide resonance structures, first proposed by Wittig, are also relevant in an evaluation of anionic di-ylide systems: $(R_2C)^-{-}(R'_2P){=}(CR_2) \leftrightarrow (R_2C)^-{-}(R'_2P)^+{-}(CR_2)^- \leftrightarrow (R_2C){=}(R'_2P)^+{-}(CR_2)^-$.

Calculated (NPA)[13] charges on the hypothetical di-ylide anion $H_2P(CH_2)_2^-$ show the charge separation $H_2P(+0.923)/CH_2(-0.962)$. This charge separation in the hypothetical dibenzylide anion $H_2P(CHPh)_2^-$ is even larger: $H_2P(+1.088)/CHPh(-1.044)$. The nearly flat geometry at the benzylidic carbon (angle of the P−C vector with the C−P−H plane is 9.1°) suggests delocalization of this negative charge in the benzylidic π-system. However, the calculated NPA charges show a strong localization of the negative charge on the benzylidic carbon. Comparison of the charge distributions in $PhCH_2^-$ and $PhCH(PH_2)^-$ (also shown in Figure 4) nicely shows the charge-localizing effect of a PH_2 substituent alone (second-row elements stabilize a negative charge at the α-position).[14] The charge localization in $H_2P(CHPh)_2^-$ is even more extreme due to additional Coulombic attraction by the positively charged PH_2^+.

This localization of negative charge on the benzylidic carbon in dibenzylide anions is also nicely demonstrated

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[11] Schmidbaur, H.; Deschler, U.; Milewski-Mahrla, B.; Zimmer-Gaser, B. *Chem. Ber.* **1981**, *114*, 608.

[12] The $^1J(C,H)$ values in methane and ethylene are 125 and 156 Hz, respectively: Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C NMR Spektroskopie*; Georg Thieme Verlag: Stuttgart, Germany, 1984.

[13] Mulliken population analyses fail to give a useful and reliable characterization of the charge distribution in many cases, especially when highly ionic compounds are involved. Charges calculated according to the natural population analysis (NPA) do not show these deficiencies and are relatively basis set independent. NPA analysis: (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Curtis, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

[14] (a) Lehn, J.-M.; Wipff, G. *J. Am. Chem. Soc.* **1976**, *98*, 7498. (b) Thatcher Borden, W.; Davidson, E.; Andersen, N. H.; Denniston, A. D.; Epiotis, N. D. *J. Am. Chem. Soc.* **1978**, *100*, 1604. (c) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467.

Table 2. Geometry (Angles in deg and Distances in Å) and Charge Distribution[a] in Benzyl Anion Systems

compd		∠ ipso	∠ ortho[b]	∠ meta[b]	∠ para	$C_\alpha-C_i$	$C_i-C_o{}^b$	$C_o-C_m{}^b$	$C_m-C_p{}^b$	$Q(\alpha)$	$Q(\text{ortho})^b$	$Q(\text{para})$
$PhCH_2^-$	calcd	113.6	122.5	122.6	116.4	1.382	1.445	1.373	1.402	41	16	27
$PhCH_2K$	X-ray[15]	113.2(2)	122.7(2)	122.2(2)	117.2(2)	1.381(3)	1.444(3)	1.375(3)	1.392(3)			
$PhCH(PH_2)^-$	calcd	114.4	122.0	122.2	117.0	1.412	1.426	1.383	1.392	62	10	17
$H_2P(PhCH)_2^-$	calcd	115.5	122.0	121.6	117.6	1.435	1.416	1.382	1.392	72	7	13
$(pbb)_2Ba$ (**8**)	X-ray	115.1(6)	121.9(6)	122.3(7)	116.7(7)	1.414(10)	1.418(10)	1.385(10)	1.388(10)			

[a] Charges are given as group charges (charge of heavy atom plus attached hydrogens) shown as a percentage of the sum of charges on C_α, C_o, and C_p. [b] For asymmetric structures with two different ortho and meta carbons, the average value is tabulated.

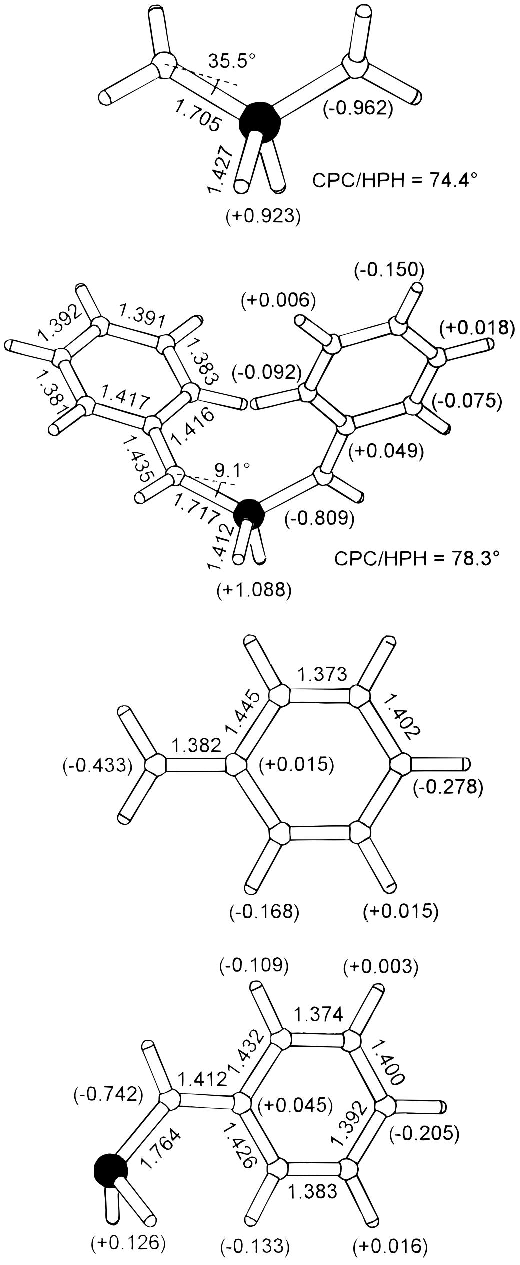

Figure 4. 4. *Ab initio* (RHF/6-31+G*) geometries and NPA charges for $H_2P(CH_2)_2^-$ (C_2), $H_2P(PhCH)_2^-$ (C_2), the benzyl anion (C_{2v}), and the benzyl$-PH_2$ anion (C_s). Charges are given in parentheses as group charges (charge of heavy atom plus attached hydrogens).

by deformation of the benzyl ring geometries as in $(pbb)_2Ba$. The characteristic distortions in the geometry of benzyl anions is related to the extent of π-delocalization and can be easily deduced from the possible resonance structures.[15] Typical effects are short $C_\alpha-C_{ipso}$ and long $C_{ipso}-C_{ortho}$ bond distances (the effect of π-delocalization on $C_{ortho}-C_{meta}$ and $C_{meta}-C_{para}$ is less pronounced). Also, C−C−C bond angles significantly deviating from 120° can be observed: characteristic is a considerable squeezing at C_{ipso} and C_{para} and a concomitant, moderate widening at C_{ortho} and C_{meta}. Table 2 shows that such distortions in $PhCH_2^-$ indeed can be considerable and that they fit quite well with those found in the X-ray structure of the highly ionic $PhCH_2^-K^+$.[15] A PH_2 substituent on the C_α atom effectively localizes charge, thus diminishing π-delocalization; a less extreme ring deformation is the consequence (Table 2). Since charge delocalization is even less in $H_2P(CHPh)_2^-$, a smaller deformation of the benzyl ring is observed. Although the geometry of the benzyl rings in $(pbb)_2Ba$ (averaged over four crystallographically different benzyl rings) has not been very accurately determined, it fits well with that calculated for the H_2P(benzylide)$_2$ anion (Table 2). Therefore, the electron distribution in $(pbb)_2Ba$ is likely quite similar to that calculated for $H_2P(CHPh)_2^-$.

The calculated and experimentally observed di-ylide anions presented here are all characterized by a typical distortion of the P bonding geometry from a tetrahedral environment. For example, in $H_2P(CH_2)_2^-$ the C−P−H bond angle for the H anti to the ylidic lone pair is larger (121.2°) than that for the gauche H (100.4°). Therefore, the angle between the PH_2 plane and the PC_2 plane (angle 74.4°) is severely distorted from the 90° angle expected in a tetrahedral conformation (plots in Figure 4 are projections on the C−P−C plane and clearly show this distortion). Similar, but smaller, distortions are observed in $H_2P(CHPh)_2^-$ (angle H_2P/PC_2 is 78.3°) and in $(pbb)_2Ba$ (angle $(C_{Ph})_2P/P(C_{benzylide})_2$ is 84.0°: this is particularly evident in the projection along the 2-fold axis depicted in Figure 3). This deformation typical for di-ylide anions has the same origin as the distortion of the P bonding geometries in P-ylides. The structures of P-ylides are characterized by a tilting of the PR_3 group with respect to the P−C axis,[16] a deformation which improves $C^-\rightarrow\pi^*(PR_3)$ negative hyperconjugation by enlargement of the C "lone pair"/$\pi^*(PR_3)$ overlap (see Figure 5a). In di-ylide anions, rotation of the PR_2 plane with respect to the PC_2 plane similarly improves negative hyperconjugation by enlargement of "lone-pair"/$\pi^*(PH_2)$ overlap (see Figure 5b). The extent of this distortion, which is related to the ylene character of the

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(15) Hoffmann, D.; Bauer, W.; Hampel, F.; van Eikema Hommes, N. J. R.; Schleyer, P. v. R.; Otto, P.; Pieper, U.; Stalke, D.; Wright, D.; Snaith, R. *J. Am. Chem. Soc.* **1994**, *116*, 528.

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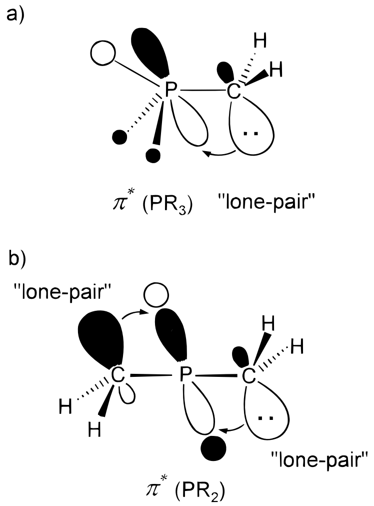

Figure 5. 5. (a) $R_3PCH_2^-$, where tilting of the PR_3 group with respect to the P−C axis improves $CH_2^- \rightarrow \pi^*$ (PR_3) negative hyperconjugation by enlargement of the CH_2 "lone pair"/π^* (PR_3) overlap. (b) $R_2P(CH_2)_2^-$, where rotation of the R_2P plane with respect to the PC_2 plane improves negative hyperconjugation by enlargement of "lone pair"/ π^* (PH_2) overlap.

P−C bond,[17] decreases along the series $H_2P(CH_2)_2^-$ > $H_2P(CHPh)_2^-$ > $(pbb)_2Ba$.

Conclusions

The S_4-symmetric solid-state structure of $(pbb)_2Ba$ (**8**) shows fluxional behavior in solution, which is ascribed to fast exchange between the two antipodes of the chiral C_2-symmetric pbb ligand.

Ab initio NPA charges show that in di-ylide anions a great extent of the negative charge is on the ylidic substituents. In the dibenzylide anion, this charge is hardly delocalized in the phenyl ring but is found mainly on the ylidic carbon next to the positively charged P. Analysis of the benzyl ring geometries in $(pbb)_2Ba$ shows that the characteristic ring distortions, which are related to the charge distribution, fit well with those calculated for the $H_2P(\text{benzylide})_2$ anion. Thus, a similar charge distribution in $(pbb)_2Ba$ is expected. However, a typical distortion of the P bonding from a tetrahedral geometry, due to $C^- \rightarrow \pi^*$ (PR_2) negative hyperconjugation, shows that the ylene character in the P−C(ylide) bonds is not negligible.

Experimental Section

General methods. All experiments were carried out under argon using predried solvents and Schlenk techniques. NMR spectra were recorder on a Bruker AC250 (250 MHz) machine. $Ba[N(TMS)_2]_2$ was prepared according to a literature procedure.[18]

Computational methods. All geometries were fully optimized within the designated symmetry constraints at the restricted Hartree−Fock level by using gradient optimization techniques and the standard basis set, 6-31+G*, incorporated in the GAUSSIAN 94 program system.[19] All stationary points were checked to be real minima by frequency analyses (no imaginary frequencies were found). Charges have been calculated by use of natural population analysis (NPA).[13]

Synthesis of 6. A solution of (4-methylbenzyl)diphenylphosphine (6.0 g, 20.7 mmol) and 4-methylbenzyl bromide (4.20 g, 22.7 mmol) in 50 mL of acetone was refluxed for 6 h. The solvent of the resulting reaction solution was removed under vacuum, and the residual white substance was crystallized by cooling a hot saturated THF/hexane (1/1) solution to −80 °C (yield 6.5 g; 66%). ^{1}H NMR ($CDCl_3$, 20 °C): δ 2.14 (s, 6H, Me); 4.82 (d, ^2J(H,P) = 15.0 Hz, 2H, ylide H); 6.82 (s, 8H, benzyl ring H's); 7.40−7.65 (m, 10 H, phenyl H's).

Synthesis of 7. A solution of of $KN(SiMe_3)_2$ (1.09 g, 5.46 mmol) in 15 mL of THF was added within 15 min to a cooled (−70 °C) suspension of the phosphonium bromide **6** (2.60 g, 5.47 mmol) in 25 mL of THF. After addition, the temperature was raised within 15 min to +20 °C and the resulting orange suspension was stirred for 1 h. The solvent was removed under vacuum (0.01 Torr) and the remaining solid was extracted two times with 10 mL portions of warm benzene. Removing the solvent from the combined benzene layers under vacuum gave an orange powder (1.90 g, 88%). A ^{1}H NMR spectrum of this product showed broad signals for the benzylic and benzylidic protons. This is due to fast proton transfer from the benzyl to the benzylide group, interconverting these functionalities. This process is catalyzed by small quantities of $HN(SiMe_3)_2$ and generally observed in ylide compounds.[11] The pure crystalline product, which can be obtained by crystallization from hexane/toluene, showed static behavior and sharp resonances. ^{1}H NMR (C_6D_6, 20 °C): δ 2.02 (s, 3H, Me); 2.23 (s, 3H, Me); 2.51 (d, ^2J(H,P) = 17.6 Hz, 1H, ylide H); 3.49 (d, ^2J(H,P) = 13.0 Hz, 2H, CH_2); 6.75−7.00 (m, 14 H, aromatic H's); 7.52 (m, 4H, Ph_{ortho}).

Synthesis of $(pbb)_2Ba$. A solution of 0.89 g (2.26 mmol) of **7** and 0.52 g (1.14 mmol) of $Ba(N(SiMe_3)_2)_2$ in 10 mL of THF was stirred for 1 h at +60 °C. The solvent of the resulting red solution was removed under vacuum and the remaining solid was freed of $HN(SiMe_3)_2$ under vacuum (0.01 Torr, 60 °C, 30 min). The orange-red solid obtained was nearly pure product but could be further purified by dissolving it in a mixture of hexane (8 mL) and toluene (8 mL) at +60 °C and cooling it slowly (within 24 h) to −20 °C. Large blocks of orange crystals were formed in an overall yield of 81% (0.85 g, 0.92 mmol). The crystals contain toluene: $(pbb)_2Ba$/toluene $\approx$ 1/1. ^{1}H NMR (toluene-d_8, 20 °C): δ 2.03 (s, 6H, Me); 2.86 (d, ^2J(H,P) = 18.0 Hz, 2H, $CH_{benzylide}$); 6.42 (s broad, 4H, *p*-tolyl ring H's); 6.68 (s broad, 4H, *p*-tolyl ring H's); 6.88−7.05 (m, 6H, $Ph_{meta/para}$); 7.86 (m, 4H, Ph_{ortho}). ^{1}H NMR (toluene-d_8, −50 °C): δ 1.96 (s, 3H, Me); 2.14 (s, 3H, Me); 2.87 (d, ^2J(H,P) = 18.0 Hz, 2H, $CH_{benzylide}$); 6.25−7.10 (several broad overlapping doublets and multiplets, 14H, *p*-tolyl ring + $Ph_{meta/para}$ H's); 7.87 (m, 4H, Ph_{ortho}). ^{1}H NMR (THF-d_8, 20 °C): δ 2.06 (s, 6H, Me); 2.57 (d, ^2J(H,P) = 15.3 Hz, 2H, $CH_{benzylide}$); 6.31 (d , ^3J(H,H) = 8.0 Hz, 4H, *p*-tolyl ring H's); 6.44 (d, ^3J(H,H) = 8.0 Hz, 4H, *p*-tolyl ring H's); 7.19−7.28 (m, 6H, $Ph_{meta/para}$); 7.75 (m, 4H, Ph_{ortho}). ^{13}C NMR (THF-d_8, 20 °C): δ 20.6 (Me); 34.1 (d, ^1J(C,P) = 115.2 Hz, $C_{benzylide}$); 120.2 (d, ^3J(C,P) = 12.3 Hz, ortho benzylide); 122.8 (para benzylide); 128.8 (d, ^3J(C,P) = 10.8 Hz, Ph_{meta}); 130.4 (Ph_{para}); 131.7 (meta benzylide); 132.3 (d, ^2J(C,P) = 9.2 Hz, Ph_{ortho}); 135.2 (d, ^1J(C,P) = 75.2 Hz, Ph_{ipso}); 146.7 (d, ^2J(C,P) = 5.4 Hz, ipso benzylide).

Crystal structure data for $(pbb)_2Ba$ (8): monoclinic, a = 14.645(3) Å, b = 12.873(1) Å, c = 26.949(6) Å, β = 93.96(1)°, V = 5068(2) Å^3, space group $P2_1/n$, formula $(C_{28}H_{26}P)_2$

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Ba$\cdot$0.70C_7H_8, $M_r = 988.8$, $Z = 4$, $\rho_{calcd} = 1.296$ g cm^{-3}, μ(Mo Kα) = 0.885 mm^{-1}; 9252 reflections measured (Mo Kα, graphite monochromator, $T = -120$ °C), 8876 unique reflections after merging ($R_{int} = 0.045$), 5689 observed reflections with $I > 2.0\sigma(I)$; solution by direct methods with the program DIRDIF,[20] full-matrix least-squares refinement (SHELXL93)[21] on F^2 to R1 = 0.058, wR2 = 0.1481 (629 parameters, 34 restraints, 8876 data). Non-hydrogen atoms were refined anisotropically; part of the hydrogens have been taken from the difference Fourier map, the rest were calculated. The benzylidic hydrogens were found and refined with a free isotropic displacement parameter. The crystals of (pbb)$_2$Ba have holes between the monomeric units. These holes, located around the inversion centers, contain disordered toluene molecules which easily evaporate from the crystal surface. The disorder model was refined with several restraints on C$\cdots$C bonding and nonbonding distances. The relatively high residual electron density of 1.73 e/Å^3 found in the area of disordered toluene molecules indicates an incomplete description of the disorder. Plots and geometry calculations were made with the EUCLID-package.[22]

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Supporting Information Available: Tables giving crystal data and structure refinement details, atomic coordinates, bond distances and angles, torsion angles, and thermal parameters for (pbb)$_2$Ba (14 pages). Ordering information is given on any current masthead page.

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