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Syntheses, Structures, and Reactivity of Barium Carbene Complexes with Chelating Bis-iminophosphorano Arms

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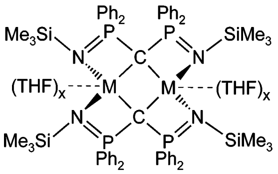
Reaction of $(Me_3SiN{=}PPh_2)_2CH_2$ with $Ba[N(SiMe_3)_2]_2$ in 1:1 ratio gave only monodeprotonation and the homoleptic product $[(Me_3SiN{=}PPh_2)_2CH]_2Ba$ (**3-Ba**) was formed. Reaction with the strong base dibenzylbarium gave fast and clean 2-fold deprotonation and the dimeric complex $[(Me_3SiN{=}PPh_2)_2CBa{\cdot}THF]_2$ (**1-Ba**) was isolated. Also the bulkier ligand $(2{,}6\text{-}i\mathrm{Pr}_2C_6H_3{-}N{=}PPh_2)_2CH_2$ was doubly deprotonated by this reagent, which gave clean formation of the monomeric complex $(2{,}6\text{-}i\mathrm{Pr}_2C_6H_3{-}N{=}PPh_2)_2CBa{\cdot}(THF)_3$ (**2-Ba**). Although organobarium compounds generally show high reactivity, the monomeric barium carbene complex **2-Ba** reacted sluggishly with benzophenone or adamantyl cyanide and reaction products could not be identified. Reaction of **2-Ba** with cyclohexyl isocyanate, however, cleanly gave the [2+2]-cycloaddition product, which crystallized as a dimer (**4**). Crystal structures of monomers **2-Ba** and **3-Ba** and dimers **1-Ba** and **4** show in all cases tridentate (*C*, *N*, *N′*)-coordination of the bis-iminophosphorano ligand. In some cases the large coordination sphere of Ba^{2+} was saturated by agostic $i\mathrm{Pr}{\cdots}Ba^{2+}$ and $\pi\text{-}\mathrm{Ph}{\cdots}Ba$ contacts.

Introduction

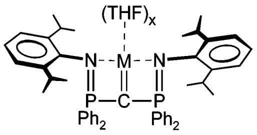
The heavier elements Ca, Sr, and Ba can be regarded as "sleeping beauties" in the organometallic chemistry of group II. One hundred years after the discovery of Grignard reagents, research activities on the chemistry of this heavy triad are finally on the increase.[1]

Although this is particularly true for calcium, the organometallic chemistry of barium is still much less explored. This is likely due to its considerable ionic radius (1.49 Å for CN = 6),[2] consequently resulting in highly reactive compounds of limited solubility. Besides its alkoxides,[3] cyclopentadienides,[4] amides, and phosphides (including ate complexes),[5] only very few crystal structures of pure Ba-carbyls have been published.[6−9] In a phosphonium dibenzylide complex, $[Ph_2P(CHAr)_2]_2Ba$,[6] the Ba^{2+} ion is nicely shielded by bonding with two bulky bidentate ligands. Saturation of the considerable coordination sphere of Ba^{2+} in the acetylide complex $(Ph_3SiC{\equiv}C)_2Ba{\cdot}$(18-crown-6)[7] is achieved by coordination of a large crown ether. The first well-defined alkylbarium compound could be obtained by electronic and steric stabilization of the alkyl anion $[(Me_3Si)_2(MeOSiMe_2)C]_2Ba{\cdot}(DME)$,[8] and recently a homoleptic barium complex with bulky bis-iminophosphoranomethyl ligands was isolated, $[(ArN{=}PPh_2)_2CH]_2Ba$.[9]

We present here the synthesis and structures of barium carbene complexes with chelating bis-iminophosphorano arms (**1-Ba** and **2-Ba**). The recently published calcium carbene analogues (**1-Ca** and **2-Ca**) could be regarded as predominantly ionic complexes with a considerable negative charge on the central carbon atom (−1.78).[10,11]



1-M
M = Ca, x = 0
M = Ba, x = 1



2-M
M = Ca, x = 2
M = Ba, x = 3

Despite this high concentration of electron density, dimeric and monomeric calcium chelating carbene complexes both exhibited rather low reactivity toward ketone and nitrile functionalities. A study of the reactivity of such barium carbene complexes, which are expected to be considerably more ionic and reactive than their Ca analogues, therefore is another goal.

Results and Discussion

Deprotonation of the bis-iminophosphoranomethane ligand $(Me_3SiN{=}PPh_2)_2CH_2$ with $Ba[N(SiMe_3)_2]_2$ gave clean monodeprotonation to $[(Me_3SiN{=}PPh_2)_2CH]_2Ba$ (**3-Ba**; Scheme 1). Under no circumstances could a second deprotonation be

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(1) For recent reviews: (a) Hanusa, T. P. *Coord. Chem. Rev.* **2000**, *210*, 329. (b) Westerhausen, M. *Angew. Chem.* **2001**, *113*, 3063; *Angew. Chem., Int. Ed.* **2001**, *40*, 2975. (c) Alexander, J. S., Ruhlandt-Senge, K. *Eur. J. Inorg. Chem.* **2002**, 2761. (d) Westerhausen, M.; Gärtner, M.; Fischer, R.; Langer, J. *Angew. Chem.* **2007**, *119*, 1994; *Angew. Chem., Int. Ed.* **2007**, *46*, 1950.

(2) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(3) (a) Hubert-Pfalzgraf, L.G. *New J. Chem.* **1987**, *11*, 663. (b) Bradley, D. C. *Chem. Rev.* **1989**, *89*, 1317. (c) Hubert-Pfalzgraf, L. G. *Appl. Organomet. Chem.* **1992**, *6*, 627. (d) Herrmann, W. A.; Huber, N. W.; Priermeier, T. *Angew. Chem.* **1994**, *106*, 102.

(4) Hanusa, T. P. *Organometallics* **2002**, *21*, 2559.

(5) (a) Westerhausen, M. *Coord. Chem. Rev.* **1998**, *176*, 157. (b) Westerhausen, M. *Dalton Trans.* **2006**, 4755.

(6) Harder, S.; Lutz, M. *Organometallics* **1997**, *16*, 225.

(7) Green, D. C.; Englich, U.; Ruhlandt-Senge, K. *Angew. Chem.* **1999**, *111*, 365; *Angew. Chem., Int. Ed.* **1999**, *38*, 354.

(8) Izod, K.; Liddle, S. T.; Clegg, W. *J. Am. Chem. Soc.* **2003**, *125*, 7534.

(9) Ahmed, S. A.; Hill, M. S.; Hitchcock, P. B. *Organometallics* **2006**, *25*, 394.

(10) Orzechowski, L.; Jansen, G.; Harder, S. *J. Am. Chem. Soc.* **2006**, *128*, 14676.

(11) Orzechowski, L.; Harder, S. *Organometallics* **2007**, *26*, 2144.

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Scheme 1

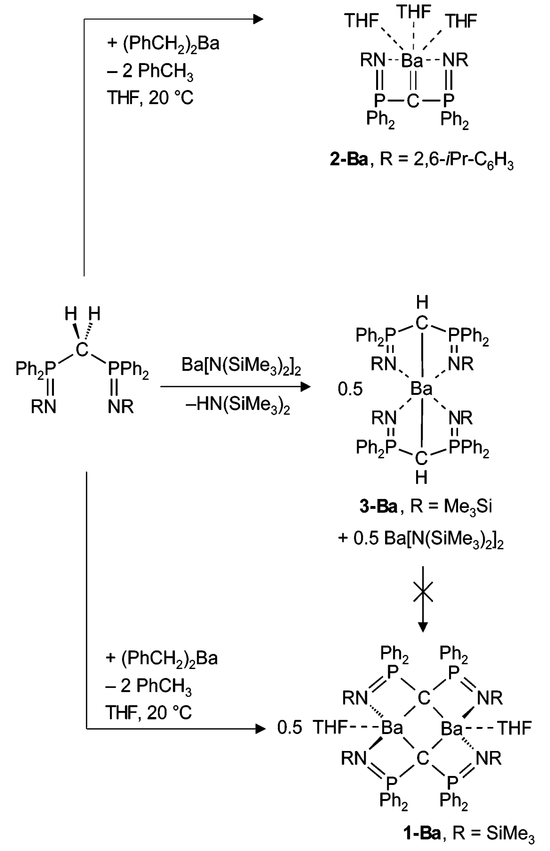

Table 1. Selected Bond Distances (Å) and Angles (deg) for 3-Ba, 1-Ba, 2-Ba, and 4

			3-Ba		
Ba−N1	2.726(2)	P1−N1	1.585(2)	N1−Ba−N2	81.38(6)
Ba−N2	2.902(2)	P2−N2	1.575(2)	C1−Ba−N1	56.51(6)
Ba−C1	3.112(3)	P1−C1	1.741(3)	C1−Ba−N2	53.70(6)
		P2−C1	1.719(3)	P1−C1−P2	127.0(2)
			1-Ba		
Ba−N1	2.759(1)	P1−N1	1.604(1)	C1−Ba−N1	55.95(3)
Ba−C1	3.144(1)	P2−N2	1.607(1)	C1−Ba′−N2	57.22(4)
Ba−C1′	2.931(1)	P1−C1	1.696(1)	Ba−C1−Ba′	87.45(3)
Ba−N2′	2.730(1)	P2−C1	1.681(1)	C1−Ba−C1′	92.55(4)
Ba−O1	2.759(2)			P1−C1−P2	130.5(1)
			2-Ba		
Ba−C1	2.918(7)	P1−N1	1.608(5)	N1−Ba−N2	109.9(2)
Ba−N1	2.685(5)	P2−N2	1.601(5)	C1−Ba−N1	57.5(2)
Ba−N2	2.631(5)	P1−C1	1.654(7)	C1−Ba−N2	57.5(2)
Ba−O1	2.856(5)	P2−C1	1.633(7)	N1−Ba−O2	92.6(1)
Ba−O2	2.867(4)	P1−C1−P2	149.7(4)	N2−Ba−O1	87.5(2)
Ba−O3	2.710(6)			N1−Ba−O3	97.0(2)
				N2−Ba−O3	110.8(2)
			4		
Ba1−O1	2.617(2)	P1−N1	1.618(2)	O1−Ba1−O2	78.21(6)
Ba1−O2	2.588(2)	P2−N2	1.620(2)	N1−Ba1−N3	165.52(6)
Ba1−N1	2.751(2)	P1−C1	1.753(3)	O1−Ba1−O3	141.45(7)
Ba1−N3	2.761(2)	P2−C1	1.749(3)	O2−Ba1−O3	140.20(7)
Ba1−O3	2.927(2)	C1−C99	1.535(3)	O1−Ba2−O2	77.09(6)
Ba2−O1	2.635(2)	C99−O1	1.328(3)	N2−Ba2−N4	113.12(7)
Ba2−O2	2.634(2)	P3−N3	1.622(2)	C1−Ba2−C50	137.04(6)
Ba2−N2	2.680(2)	P4−N4	1.614(2)	C1−Ba2−N2	55.12(7)
Ba2−N4	2.702(2)	P3−C50	1.758(3)	C50−Ba2−N4	55.17(6)
Ba2−C1	3.177(3)	P4−C50	1.753(3)	P1−C1−P2	126.0(1)
Ba2−C50	3.163(3)	C50−C106	1.538(4)	P3−C50−P4	125.3(1)
		C106−O2	1.332(3)		

observed, which suggests that the pK_{a2} of this ligand is higher than 25.8, i.e., the pK_a of $HN(SiMe_3)_2$.[12]

Complex **3-Ba** crystallized as a crystallographically C_2-symmetric monomer (Figure 1; Table 1), and, although not isomorphous, its molecular structure is very similar to that of the calcium analogue **3-Ca**.[10] Despite the large difference in ionic radii between Ca^{2+} and Ba^{2+} (for six-coordinate cations, radii of 1.14 and 1.49 Å have been reported, respectively),[2] **3-Ba** also crystallizes from a hexane/THF mixture without coordinated THF ligands. This reflects the enormous bulk and flexibility of the bis-iminophosphoranomethyl ligand and underscores its recent definition as a hemilabile ligand system[9] that easily adapts itself to the metal. The Ba^{2+} ion in **3-Ba** is 6-fold coordinated by the two tridentate ligands, and although there are gaps in the coordination sphere, there are neither obvious agostic SiMe$\cdots$$Ba^{2+}$ interactions nor π-Ph$\cdots$$Ba^{2+}$ contacts. The structure compares well to that of a closely related barium complex, $[(\text{mesityl-N}{=}PPh_2)_2CH]_2Ba$,[9] which also crystallized as a THF-free C_2-symmetric monomer. Although the bis-iminophosphoranomethyl ligands in both complexes are only slightly different, i.e., a Me_3Si substituent versus a mesityl group, their ligand−metal coordination geometries display large discrepancies. Whereas in the mesityl-substituted complex the Ba−C distances (3.949(3) and 3.580(4) Å) are too large to be defined as Ba−C bonds, in **3-Ba** a distinctive bonding interaction between Ba^{2+} and the methanide carbon is recognized (3.112(3) Å). This bond length is essentially equal to that of 3.127(3) Å in the iodide-bridged dimer $[(Me_3SiN{=}PPh_2)_2C(H)Ba(\mu\text{-}I)]_2$.[13] The Ba−C bond in **3-Ba** is considerably longer than the average Ba−C bond of 2.853(3) Å in the acetylide complex $(Ph_3SiC{\equiv}C)_2Ba\cdot$(18-crown-6),[7] but compares well to the average Ba−C distances of 3.043(2) and 3.153(4) Å in the tris-silylated alkyl complex $[(Me_3Si)_2(MeOSiMe_2)C]_2Ba\cdot(DME)$[8] and the phosphonium dibenzylide complex $[Ph_2P(CHC_6H_4\text{-}4\text{-}Me)_2]_2Ba$,[6] respectively. Also, the 0.347 Å difference between the carbon−metal bonds in **3-Ca** and **3-Ba** compares well to the 0.35 Å difference in ionic radii of Ca^{2+} and Ba^{2+}.

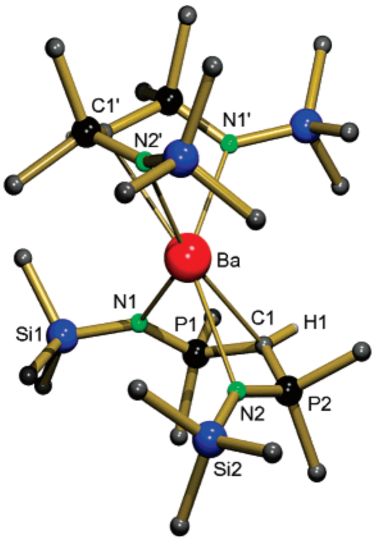

Figure 1. Crystal structure of **3-Ba**. For clarity all hydrogen atoms (except H1, which has been located and refined) and phenyl substituents (except C_{ipso}) have been omitted. Selected bond distances and angles are given in Table 1.

The Ba−N bonds in **3-Ba** display the same discrepancy as observed for **3-Ca**; that is, one of the contacts (2.726(2) Å) is considerably shorter than the other (2.902(2) Å). The shorter

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(12) Fraser, R. R.; Mansour, T. S.; Savard, S. *J. Org. Chem.* **1985**, *50*, 3232.

(13) Panda, T. K.; Zulys, A.; Gamer, M. T.; Roesky, P. W. *J. Organomet. Chem.* **2005**, *690*, 5078.

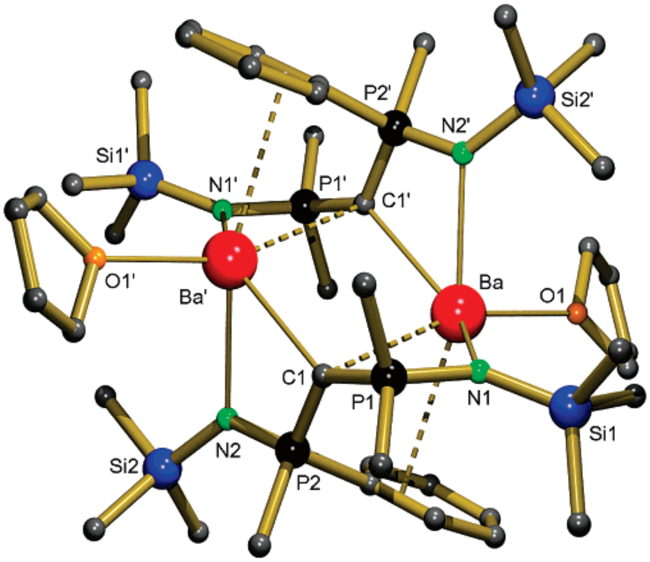

Figure 2. Crystal structure of **1-Ba**. For clarity all hydrogen atoms and phenyl substituents (except the C_{ipso} atoms and the ring involved in π-Ph···Ba coordination) have been omitted. Selected bond distances and angles are given in Table 1.

contact compares well to the average Ba−N bond of 2.712(2) Å in the β-diketiminate complex $[CH\{(CMe)(2,6\text{-}i Pr_2C_6H_3N)\}_2]_2Ba$.[14] Elongation of the other Ba−N bond might be ascribed to steric interactions between the two bulky ligands coordinating at a mutual metal center (discrepancy of the Ca−N bonds in **3-Ca** was explained similarly).[10] The average value of the Ba−N bonds in **3-Ba** (2.815(2) Å) is comparable to that in $[(Me_3SiN{=}PPh_2)_2C(H)Ba(\mu\text{-}I)]_2$, a complex that shows less discrepancy in Ba−N bond lengths: values of 2.784(2) and 2.866(3) Å were observed (average: 2.825(3) Å).[13] The difference between the metal−nitrogen bond lengths in **3-Ca** and **3-Ba** of 0.266 Å is considerably smaller than the 0.35 Å difference in the ionic radii of their metal centers.

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **3-Ba** dissolved in C_6D_6 all show one set of signals for the $Me_3SiN{=}(Ph)_2P$ substituents. This means that the inequivalence of these substituents, as shown in the crystal structure, is averaged by fast rotation of the ligands with respect to each other. The ^{13}C NMR signal for the central carbon atom appeared as a triplet at 21.6 ppm ($^1J_{C,P} = 118$ Hz) and compares well to that in **3-Ca** (23.4 ppm; $^1J_{C,P} = 109$ Hz).[10]

Fast and clean 2-fold deprotonation of the bis-iminophosphoranomethane ligand $(Me_3SiN{=}PPh_2)_2CH_2$ (Scheme 1) could be achieved by using the strongest accessible organobarium base, dibenzylbarium, for which recently a convenient synthetic pathway was introduced.[15] Product **1-Ba** is easily soluble in THF and crystallized as a colorless compound of formula $[(Me_3SiN{=}PPh_2)_2CBa{\cdot}THF]_2$.

A crystal structure determination of **1-Ba** revealed a crystallographically centrosymetric dimer in which the $(Me_3SiN{=}PPh_2)_2C^{2-}$ ligands bridge the Ba^{2+} ions (Figure 2; Table 1). The coordination sphere of Ba^{2+} is saturated by an additional THF ligand bound in terminal position. Whereas the $(Me_3SiN{=}PPh_2)_2C^{2-}$ ligands in the comparable dimeric calcium complex **1-Ca** bridge symmetrically, the present structure shows a rather asymmetric bridging with Ba−C bond distances of 2.931(1) and 3.144(1) Å. Formally, the shorter Ba−C bond corresponds to interaction of Ba^{2+} with a filled sp^2-orbital (the angle between the Ba′−C1 vector and the PCP plane is 0.6(1)°), whereas the longer bond represents interaction with a filled p-orbital (the angle between the Ba−C1 vector and the PCP plane is 80.0(1)°). The significantly longer Ba−C1(p) bond is in line with the larger radial extension of the p-orbital.

The $(RN{=}P{-}C{-}P{=}NR)^{2-}$ ligand is severely distorted from a planar W geometry: the dihedral angle N2−P2−C1/C1−P1−N1 is 79.1(1)°. The reason for this distortion is the formation of an additional π-Ph···Ba^{2+} contact. One of the Ph rings binds to Ba^{2+} with Ba−C bonds of 3.307 Å (C_{ipso}) and 3.488(2)/3.522(2) Å (C_{ortho}). The Ba−C distances to other atoms in the ring are well outside the cutoff value of 3.84 Å, i.e., the sum of the van der Waals radii of Ba and C.

The average Ba−N bond of 2.745(1) in **1-Ba** compares well to that of 2.712(2) Å in the β-diketiminate complex $[CH\{(CMe)(2,6\text{-}i Pr_2C_6H_3N)\}_2]_2Ba$.[14] Average metal−C and metal−N bonds in **1-Ba** are 0.487 and 0.439 Å longer than those in the Ca analogue **1-Ca**, respectively. This is considerably more than than the 0.35 Å difference in the ionic radii of Ca^{2+} and Ba^{2+}. The longer than expected bonds to Ba are likely due to the additional π-Ph···Ba^{2+} interaction, which results in significant distortion of the ligand−Ba coordination and an increase in the effective coordination number of the metal.

The dimer **1-Ba** is only very sparingly soluble in C_6D_6. However, addition of a few equivalents of THF-d_8 increased its solubility and gave rise to the appearance of another set of signals in the ^1H NMR spectrum. These signals increased with increasing THF-d_8 addition, and in pure THF-d_8 only one set of signals could be observed again. This observation is indicative of a dimer−monomer equilibrium that is dependent on THF concentration (a similar observation has been made for **1-Ca**).[10] In pure THF-d_8 the ^{13}C NMR signal for the central carbon atom could be observed as a triplet at 53.9 ppm, a value that compares well to that observed for **1-Ca** (THF-d_8: 44.9 ppm). Its rather large $^1J_{C,P}$ of 198 Hz, however, is much larger than the value observed in **1-Ca** (THF-d_8: $^1J_{C,P} = 70$ Hz), a difference that likely is related to a different conformation of the N−P−C−P−N backbone.

Also reaction of the bulkier bis-iminophosphoranomethane ligand $(2,6\text{-}i Pr_2C_6H_3{-}N{=}PPh_2)_2CH_2$ with dibenzylbarium gave fast and clean 2-fold deprotonation (Scheme 1). The product is readily soluble in benzene and crystallized as a colorless complex with formula $(2,6\text{-}i Pr_2C_6H_3{-}N{=}PPh_2)_2CBa{\cdot}(THF)_3$ (**2-Ba**). Like **2-Ca**, also **2-Ba** is a monomeric metal chelating carbene complex in which the bis-iminophosphoranomethandiide ligand coordinates in a pincer-like fashion (Figure 3; Table 1). The larger coordination sphere of Ba^{2+} is additionally filled with three THF ligands. The bis-iminophosphoranomethandiide ligand in **2-Ba** displays the typical "open book" conformation, which has been observed in a variety of metal complexes containing such ligands.[16] The dihedral angle between the Ba−C−P−N planes of 28.5(1)° is considerably smaller than the analogous angle of 45.4(1)° in **2-Ca** but lies well in the 0−37.7° range observed in similar Ti, Zr, Hf, and Sm complexes.[16a]

The rather short Ba−C bond of 2.918(7) Å is in line with a strong bond, as expected on behalf of considerable negative charge on the carbene carbon atom.[17] Only the Ba−C bond in a barium acetylide (2.853(3) Å)[7] is shorter, which can be

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(14) Harder, S. *Organometallics* **2002**, *21*, 3782.

(15) Weeber, A.; Harder, S.; Brintzinger, H.-H.; Knoll, K. *Organometallics* **2000**, *19*, 1325.

(16) For recent reviews on metal carbene complexes with RN=P−C−P=NR ligands see: (a) Cavell, R. G.; Kamalesh Babu, R. P.; Aparna, K. *J. Organomet. Chem.* **2001**, *617−618*, 158. (b) Jones, N. D.; Cavell, R. G. *J. Organomet. Chem.* **2005**, *690*, 5485.

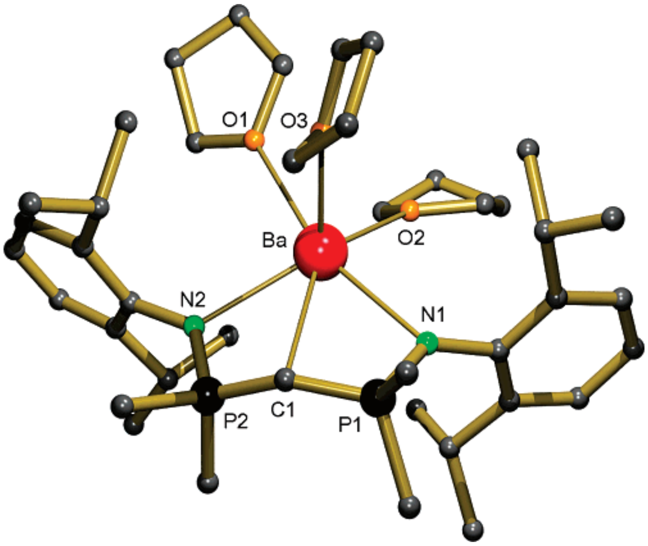


Figure 3. Crystal structure of **2-Ba**. For clarity all hydrogen atoms and phenyl substituents (except the C_{ipso} atoms) have been omitted. Selected bond distances and angles are given in Table 1.

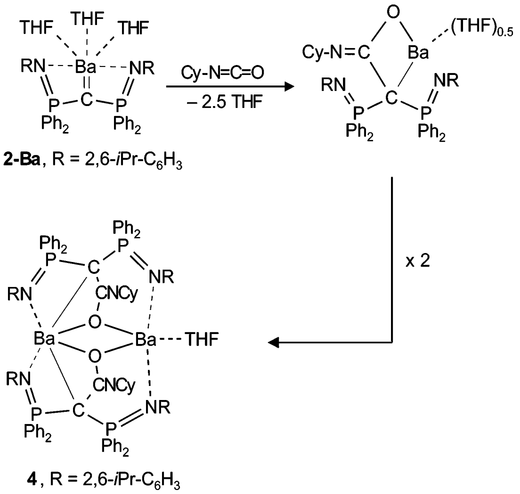
attributed to the sp-hybridization of carbon. The 0.37 Å difference between metal−carbon bonds in **2-Ca** and **2-Ba** corresponds well with the 0.35 Å difference in ionic radii of Ca^{2+} and Ba^{2+}. The average Ba−N bond of 2.658(5) Å, however, is 0.299 Å longer than the Ca−N bonds in **2-Ca** and thus shorter than expected on account of differences in ionic radii. A similar observation was made for the couple **3-Ca**/**3-Ba** (vide supra). This is in line with an earlier conclusion: the ratio of the metal−N and metal−C bond lengths increases with increasing covalency of the ligand−metal bond.[10−11,18]

The THF ligand apical to the plane of the chelating bis-iminophosphoranomethandiide ligand (O3) features a Ba−O bond that is considerably shorter than the bonds to the other THF ligands. This is likely due to steric effects: the THF ligands situated in the plane of the chelating ligand (O1 and O2) are more crowded.

Crystals of **2-Ba** dissolve well in C_6D_6. Atypically, only one doublet for the *i*Pr methyl groups is observed in the ^{1}H NMR spectrum. This indicates fast rotation of the 2,6-iPr$_2$C$_6$H$_3$ ring around the C−N bond already at room temperature. Cooling a solution of **2-Ba** in toluene-d_8 gave decoalescence in two doublets for the two different Me groups facing either the metal or the Ph$_2$P moiety. The activation energy for this aryl ring rotation in **2-Ba** ($\Delta G^{\ddagger} = 12.6(1)$ kcal mol^{-1}, $T_{coal} = -15$ °C) is lower than that estimated for **2-Ca** ($\Delta G^{\ddagger} = 15.5(1)$ kcal mol^{-1}, $T_{coal} = 40$ °C). Whereas the ^{13}C NMR signal for the carbene carbon atom in **2-Ca** could not be found,[11] a weak resonance is observed for the carbene carbon in **2-Ba**: 47.4 ppm, $^1J_{C,P} = 157.1$ Hz.

The reactivity of the monomeric barium carbene **2-Ba** toward unsaturated bonds was tested by reactions with ketone, nitrile, and isocyanate substrates. Addition of benzophenone to monomer **2-Ba** gave the typical color change to red, which was earlier observed for the coordination complex of **2-Ca** with benzophenone and was attributed to charge transfer.[11] Although **2-Ba** and benzophenone slowly reacted at 60 °C, complete conversion was never reached (not even after 3 days). Incomplete conversion as well as decomposition processes complicated the isolation of reaction products, which thus far are unidentified. The same sluggish reaction behavior was found in reactions with adamantyl cyanide.

Scheme 2



Reaction of **2-Ba** with cyclohexyl isocyanate, however, gave already at room temperature a clean [2+2]-cycloaddition, and crystals of a product with composition $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{−N═PPh}_2)_2\text{C−C(═N-Cy)O}]_2\text{Ba}_2\cdot\text{THF}$ (**4**) could be isolated in 57% yield (Scheme 2). The crystal structure (Figure 4, Table 1) shows a dimeric complex of approximate C_2-symmetry in which the Ba^{2+} ions are symmetrically bridged by oxygens (O1 and O2). Whereas the iminophosphorano substituents coordinate with the nitrogens in a chelating fashion, the CyN═C functionality is not bound to Ba. This is in contrast to an earlier reported structure of a similar dimeric calcium complex, $[(\text{Me}_3\text{Si−N═PPh}_2)_2\text{C−C(═N-Cy)OCa}]_2$, in which the CyN═C(O) unit functions as an (*N*, *O*)-bidentate bridge between the Ca^{2+} ions.[10]

For Ba1, the coordination sphere is further saturated by a THF ligand and can be described as trigonal bipyramidal. The Ba−O3 bond of 2.927(2) Å is rather long, probably due to steric repulsion with four *i*Pr substituents. The Ba−THF interaction

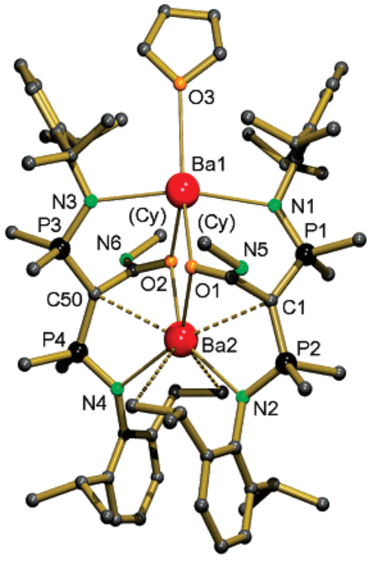


Figure 4. Crystal structure of **4**. For clarity all hydrogen atoms, the cyclohexyl substituents (except C_{α}), and the phenyl substituents (except C_{ipso}) have been omitted. Selected bond distances and angles are given in Table 1.

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(17) For the model complex $(\text{HN═PH}_2)_2\text{CCa}$, which shows a similar open book conformation, the calculated NPA charge on the carbene carbon is −1.629 (B3LYP/TZVPP).[10]

(18) Eaborn, C.; Hill, M. S.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **2002**, 2467.

results in a tilting of the bis-iminophosphoranomethanide ligand and shuts off Ba2 for interaction with additional THF ligands. Ba2 is coordinatively saturated by bonding to the central carbons of the bis-iminophosphoranomethanide ligands with bond lengths of 3.163(3) and 3.177(3) Å, i.e. at the higher range for Ba−C bonding. In addition, agostic interactions between *i*Pr substituents and Ba2 are observed with Ba···H distances varying from 2.88 to 2.98 Å (accompanying Ba···C distances: 3.565(4)−3.722(4) Å). Thus, the distorted tetrahedral coordination sphere around Ba2, spanned by O1, O2, N2, and N4, is penetrated by an additional tetrahedral coordination sphere, which consists of weaker bonds to C1 and C50 and two agostic interactions.

Conclusions

Since attempts to deprotonate bis-iminophosphoranomethane ligands with $Ba[N(SiMe_3)_2]_2$ only gave monodeprotonation, the pK_{a2} for such ligands is greater than 25.8. However, barium carbene complexes with chelating iminophosphorane substituents are easily accessible by 2-fold deprotonation of such ligands with the strong base dibenzylbarium.

The structure of monodeprotonated complex **3-Ba** is very similar to that of its Ca analogue **3-Ca**, which reflects the enormous bulk and flexibility of the bis-iminophosphoranomethyl ligand. Structures of the dimeric carbene complexes **1-Ca** and **1-Ba** show more discrepancies, which are particularly determined by π-Ph···Ba^{2+} interactions. Increasing the size of the imino substituents, i.e., replacing a Me_3Si for a 2,6-iPr-phenyl substituent, prevents formation of dimeric complexes, and even for the considerably larger Ba^{2+} a monomeric carbene complex **2-Ba** could be isolated.

Although the reactivity of organometallic complexes of the alkaline-earth metals increases considerably down the series Be−Ba, even a barium carbene complex with chelating iminophosphorane substituents reacted slowly with ketones and nitriles and [2+2]-cycloaddition could be observed only with a highly electrophilic isocyanate. In contrast, the recently published samarium carbene anion $\{[(S{=}PPh_2)_2C]_2Sm^{III}\}^-$ reacted smoothly with benzophenone.[19] The reason for sluggish reactivity of the here presented barium carbenes probably originates from (i) steric shielding of the metal−carbene bond, which is much less in $\{[(S{=}PPh_2)_2C]_2Sm^{III}\}^-$, and (ii) the stabilizing influence of two positively charged phosphonium neighbors, which are likely less positive in the anion $\{[(S{=}PPh_2)_2C]_2Sm^{III}\}^-$. Higher reactivity of the Sm^{III} carbene could also be due to the considerably more Lewis acidic metal center, which activates the ketone for nucleophilic attack.

Experimental Section

All experiments were carried out using standard Schlenk techniques and freshly dried solvents. The barium carbenes **1-Ba** and **2-Ba** are extremely moisture sensitive and very reactive toward protic species. Therefore all solvents used for this compound were dried and stored over Na/K alloy. The following compounds were prepared according to the literature $(Me_3SiN{=}PPh_2)_2CH_2$,[20] (2,6-iPr$_2$C$_6$H$_3$−N=PPh$_2$)$_2$CH$_2$,[21] $Ba[N(SiMe_3)_2]_2$,[22] and dibenzylbarium.[15] NMR spectra were measured on a Bruker DPX300 or DRX500 spectrometer. Crystals were measured on a Siemens Smart diffractometer with an APEXII area detector system.

Synthesis of 1-Ba. Dibenzylbarium (0.45 g, 1.41 mmol) and $(Me_3SiN{=}PPh_2)_2CH_2$ (0.716 g, 1.28 mmol) were dissolved in 5 mL of THF. The resulting red-brown solution was stirred for 15 min at room temperature. Removal of all solvents resulted in an ocher-colored powder, which was dried under vacuum (40−50 °C, 1 Torr, 10 min). The product was washed two times with 3 mL portions of hexane and again dried under vacuum (50 °C, 1 Torr, 10 min), giving a yellow powder that is essentially pure: 0.81 g, 83%. Crystallization from a concentrated THF solution gave crystals suitable for X-ray diffraction. Anal. Calcd for $C_{70}H_{92}Ba_2N_4O_2P_4Si_4$ (M = 1532.46): C, 54.86; H, 6.05. Found: C, 54.59; H, 5.86. Mp: 185 °C (dec). ^{1}H NMR (300 MHz, THF-d_8): δ −0.21 (s, 18H, SiMe$_3$), 6.89−7.01 (m, 12H, *m*-, *p*-Ph), 7.42 (dd, $^3J_{H-H} = 6.3$ Hz, $^3J_{P-H} = 12.4$ Hz, 16H, *o*-Ph). ^{13}C NMR (75 MHz, C$_6$D$_6$): δ 4.7 (s, SiMe$_3$), 53.9 (t, $^1J_{P-C} = 197.7$ Hz, PCP), 126.8 (t, $^3J_{P-C} = 5.6$ Hz, *m*-Ph), 127.0 (s, *p*-Ph), 131.7 (t, $^2J_{P-C} = 5.4$ Hz, *o*-Ph), 147.1 (AXX′ spin system, *ipso*-Ph). ^{31}P NMR (120 MHz, THF-d_8): δ −5.37 (s, PCP).

Synthesis of 2-Ba. Dibenzylbarium (0.28 g, 0.88 mmol) and (2,6-iPr$_2$C$_6$H$_3$−N=PPh$_2$)$_2$CH$_2$ (0.585 g, 0.80 mmol) were dissolved in 6 mL of THF. After stirring the red-orange solution for 30 min at room temperature all solvents were removed under vacuum. The resulting red-orange foam was washed twice with 3 mL portions of hexane and dried under vacuum (50 °C, 1 Torr, 10 min), giving an ocher powder that is essentially pure: 0.75 g, 87%. Slowly cooling a concentrated THF solution of **2-Ba** to −28 °C resulted in clear crystals suitable for X-ray diffraction. Anal. Calcd for $C_{61}H_{78}BaN_2O_3P_2$ (M = 1086.60): C, 67.43; H, 7.24. Found: C, 67.02; H, 6.99. Mp: 209 °C (dec). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 1.03 (brs, 12H,CHMe$_2$), 1.05 (brs, 12H,CHMe$_2$), 4.05 (sept, $^3J_{H-H} = 6.6$ Hz, 4H, CHMe$_2$), 6.89 (t, $^3J_{H-H} = 7.4$ Hz, 2H, *p*-DIPP), 6.97−7.02 (brs, 12H, *m*-, *p*-Ph), 7.11 (t, $^3J_{H-H} = 7.5$ Hz, 4H, *m*-DIPP), 7.79 (dd, $^3J_{H-H} = 7.4$ Hz, $^3J_{P-H} = 11.3$ Hz, 8H, *o*-Ph). ^{13}C NMR (75 MHz, C$_6$D$_6$): δ 24.8 (brs, *i*Pr), 25.5 (s, *i*Pr) 74.4 (t, $^1J_{P-C} = 157.1$ Hz, PCP), 118.6 (s, *p*-DIPP), 123.5 (s, *m*-DIPP) 127.0 (t, $^4J_{P-C} = 5.3$ Hz, *m*-Ph), 127.5 (s, *p*-Ph), 131.8 (t, $^3J_{P-C} = 4.5$ Hz, *o*-Ph), 144.1 (m, AXX′ spin system, *ipso*-Ph), 144.8 (t, 3$J_{P-C} = 3.4$ Hz, *o*-DIPP), 150.9 (brs, *ipso*-DIPP). ^{31}P NMR (120 MHz, C$_6$D$_6$): δ −3.76 (s, PCP).

Synthesis of 3-Ba. $Ba[N(TMS)_2]_2$ (0.262 g, 0.435 mmol) and $(Me_3SiN{=}PPh_2)_2CH_2$ (0.238 g, 0,426 mmol) were dissolved in 5 mL of THF. The light yellow solution was stirred for 1 h at room temperature. The solvent was removed under vacuum. The resulting light yellow foam was dried under vacuum (40 °C, 1 Torr, 10 min) and dissolved in 2 mL of hexane and 0.4 mL of THF, and the solution was slowly cooled to −28 °C. After 2 days clear crystals (0.157 g, 58.8%) suitable for X-ray diffraction could be isolated. Anal. Calcd for $C_{62}H_{78}BaN_4P_4Si_4$ (M = 1252.92): C, 59.44; H, 6.28. Found: C, 59.21; H, 6.34. Mp: 88−89 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.17 (s, 36H, SiMe$_3$), 1.85 (t, $^3J_{P-H} = 1.5$ Hz, 2H, CH), 7.02 (s, 16H, *m*-Ph), 7.04 (s, 8H, *p*-Ph), 7.76 (dd, $^3J_{H-H} = 7.4$ Hz, $^3J_{P-H} = 9.6$ Hz, 16H, *o*-Ph). ^{13}C NMR (75 MHz, C$_6$D$_6$): δ 4.7 (s, SiMe$_3$), 21.6 (t, $^1J_{P-C} = 117.8$ Hz, CH), 127.9 (t, $^3J_{P-C} = 6.0$ Hz, *m*-Ph), 129.5 (s, *p*-Ph), 131.2 (t, $^2J_{P-C} = 5.2$ Hz, *o*-Ph), 141.0 (dd, $^1J_{P-C} = 92.2$ Hz, $^3J_{P-C} = 3.8$ Hz, *ipso*-Ph). ^{31}P NMR (120 MHz, C$_6$D$_6$): δ 14.45 (s, PCP).

Synthesis of 4. Addition of a solution of cyclohexyl isocyanate in benzene (58.0 mg of a 10 wt % solution, 46.3 μmol) to a red solution of **2-Ba** (49.8 mg, 45.8 μmol) in 0.5 mL of benzene caused an immediate color change to orange. During the reaction uniform well-defined colorless crystals precipitated from the reaction mixture, which were isolated after 1 day: 54.0 mg, 57%. The complex is completely insoluble in all common aprotic polar solvents and could therefore not be characterized by NMR. Anal.

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(19) Cantat, T.; Jaroschik, F.; Nief, F.; Ricard, L.; Mézailles, N.; Le Floch, P. *Chem. Commun.* **2005**, 5178.

(20) Appel, R.; Ruppert, I. *Z. Allge. Anorg. Chem.* **1974**, *406*, 131.

(21) Al-Benna, S.; Sarsfield, M. J.; Thornton-Pett, M.; Ormsby, D. L.; Maddox, P. J.; Brés, P.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **2000**, 4247.

(22) Vaartstra, B. A.; Huffman, J. C.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 121.

Calcd for $C_{116}H_{138}Ba_2N_6O_3P_4$ (M = 2063.01): C, 67.54; H, 6.74. Found: C, 67.44; H, 6.84. Mp: 189−190 °C (dec).

Crystal Structure Determinations. Data were collected on a Siemens SMART CCD diffractometer at −70 °C with Mo Kα radiation (0.71073 Å). Intensities were corrected for absorption using the semiempirical psi-scan method. Crystal structures have been solved by direct methods (SHELXS-97)[23] and were refined with SHELXL-97.[24] All geometry calculations and graphics have been performed with PLATON.[25] Crystallographic data (excluding structure factors) for the crystal structures of **3-Ba**, **1-Ba**, **2-Ba**, and **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 649980−649983, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for 1-Ba: $C_{70}H_{92}Ba_2N_4O_2P_4Si_4$, M_r = 1532.38, triclinic, space group $P\bar{1}$, a = 12.2767(3) Å, b = 13.7861(3) Å, c = 13.8440(3) Å, α = 79.957(1)°, β = 64.154(1)°, γ = 78.575(1)°, V = 2056.59(8) Å^3, Z = 1, ρ_{calcd} = 1.237 Mg m^{-3}, $F(000)$ = 784, μ(Mo Kα) = 1.127 mm^{-1}. Of the 203 143 measured reflections, 17 872 were independent (R_{int} = 0.033, θ_{max} = 34.9°) and 15 755 observed ($I > 2\sigma(I)$). The final refinement converged to R_1 = 0.0290 for $I > 2\sigma(I)$, wR_2 = 0.0918, and GOF = 1.10 for all data. The final difference Fourier synthesis gave a min./max. residual electron density of −0.52/+1.11 e•Å^{-3}. All hydrogen atoms have been placed on calculated positions and were refined in a riding mode. The disorder in two noncoordinating THF molecules could not be resolved properly and was treated with the SQUEEZE procedure.[26]

Crystal data for 2-Ba: $C_{61}H_{78}BaN_2O_3P_2$, M_r = 1086.52, monoclinic, space group $P2_1/n$, a = 13.8119(2) Å, b = 19.4211(3) Å, c = 22.4764(4) Å, β = 103.377(1)°, V = 5865.5(2) Å^3, Z = 4, ρ_{calcd} = 1.230 Mg m^{-3}, $F(000)$ = 2272, μ(Mo Kα) = 0.774 mm^{-1}. Of the 48 730 measured reflections, 7150 were independent (R_{int} = 0.103, θ_{max} = 22.0°) and 5631 observed ($I > 2\sigma(I)$). The final refinement converged to R_1 = 0.0589 for $I > 2\sigma(I)$, wR_2 = 0.1736, and GOF = 1.08 for all data. The final difference Fourier synthesis gave a min./max. residual electron density of −0.97/+0.95 e•Å^{-3}. All hydrogen atoms have been placed on calculated positions and were refined in a riding mode. Disorder in one of the *i*Pr substituents, a Ph substituent, and a THF ligand was treated with disorder models. The disorder in two noncoordinating THF molecules could not be resolved properly and was treated with the SQUEEZE procedure.[26]

Crystal data for 3-Ba: $C_{62}H_{78}BaN_4P_4Si_4$, M_r = 1252.85, monoclinic, space group $C2/c$, a = 13.2021(3) Å, b = 20.3922(5) Å, c = 28.6081(7) Å, β = 104.565(1)°, V = 7454.4(3) Å^3, Z = 4, ρ_{calcd} = 1.116 Mg m^{-3}, $F(000)$ = 2600, μ(Mo Kα) = 0.717 mm^{-1}. Of the 134 721 measured reflections, 10 669 were independent (R_{int} = 0.069, θ_{max} = 29.9°) and 8290 observed ($I > 2\sigma(I)$). The final refinement converged to R_1 = 0.0440 for $I > 2\sigma(I)$, wR_2 = 0.1134, and GOF = 1.07 for all data. The final difference Fourier synthesis gave a min./max. residual electron density of −0.42/+0.68 e•Å^{-3}. All hydrogen atoms have been placed on calculated positions and were refined in a riding mode. The disorder in two noncoordinating THF molecules could not be resolved properly and was treated with the SQUEEZE procedure.[26]

Crystal data for 4: $C_{116}H_{138}Ba_2N_6O_3P_4\cdot(C_6H_6)_3$, M_r = 2297.20, triclinic, space group $P\bar{1}$, a = 15.2106(8) Å, b = 17.7038(9) Å, c = 24.3033(12) Å, α = 89.555(3)°, β = 79.116(3)°, γ = 64.692(1)°, V = 5790.3(5) Å^3, Z = 2, ρ_{calcd} = 1.318 Mg m^{-3}, $F(000)$ = 2396, μ(Mo Kα) = 0.787 mm^{-1}. Of the 92 040 measured reflections, 26 243 were independent (R_{int} = 0.046, θ_{max} = 27.5°) and 20 171 observed ($I > 2\sigma(I)$). The final refinement converged to R_1 = 0.0365 for $I > 2\sigma(I)$, wR_2 = 0.1054, and GOF = 1.05 for all data. The final difference Fourier synthesis gave a min./max. residual electron density of −0.56/+0.89 e•Å^{-3}. All hydrogen atoms have been placed on calculated positions and were refined in a riding mode. Three slightly disordered benzene molecules cocrystallized: disorder was treated by refinement with relatively large displacement factors.

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Supporting Information Available: Crystal data (cif) and all figures represented in ORTEP style (doc). This material is available free of charge via the Internet at http://pubs.acs.org.

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[23] Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; Universität Göttingen: Germany, 1997.

[24] Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*, Universität Göttingen: Germany, 1997.

[25] Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2000.

[26] van der Sluis, P. A.; Spek, A. L. *Acta Crystallogr. A* **1990**, *46*, 194.