

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/255107337>

# Molecular 'Light Switch' for DNA: $\text{Ru}(\text{bpy})_2(\text{dppz})^{2+}$

ARTICLE in JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · JUNE 1990

Impact Factor: 12.11 · DOI: 10.1021/ja00168a052

CITATIONS

851

READS

80

5 AUTHORS, INCLUDING:



[Alan E Friedman](#)

University Center Rochester

51 PUBLICATIONS 2,922 CITATIONS

[SEE PROFILE](#)



[Jacqueline K Barton](#)

California Institute of Technology

390 PUBLICATIONS 31,079 CITATIONS

[SEE PROFILE](#)



[Jean-Pierre Sauvage](#)

University of Strasbourg

504 PUBLICATIONS 25,889 CITATIONS

[SEE PROFILE](#)

Molecular "Light Switch" for DNA: Ru(bpy)<sub>2</sub>(dppz)<sup>2+</sup>

Alan E. Friedman,<sup>†‡</sup> Jean-Claude Chambron,<sup>†</sup>  
Jean-Pierre Sauvage,<sup>‡</sup> Nicholas J. Turro,<sup>§</sup> and  
Jacqueline K. Barton<sup>\*,†,§</sup>

Division of Chemistry and Chemical Engineering  
California Institute of Technology  
Pasadena, California 91125

Institut de Chimie, Université Louis Pasteur  
Strasbourg, France

Department of Chemistry, Columbia University  
New York, New York 10027

Received January 8, 1990

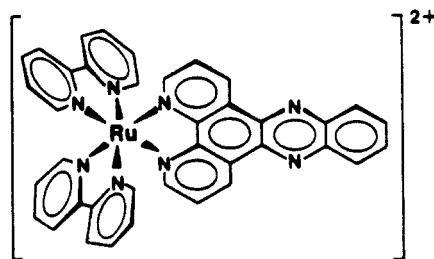
Considerable research has focused on the development of nonradioactive probes for nucleic acids.<sup>1</sup> On the basis of the well-characterized photophysical properties of ruthenium polypyridyls,<sup>2</sup> we earlier developed Ru(phen)<sub>3</sub><sup>2+</sup> (phen = 1,10-phenanthroline) and its derivatives as spectroscopic probes for DNA structure.<sup>3-5</sup> Extensive photophysical studies<sup>4</sup> indicate that Ru(phen)<sub>3</sub><sup>2+</sup> bound to double-helical DNA displays an increase in luminescence owing to intercalation; emission from the metal-to-ligand charge transfer (MLCT) excited state decays as a biexponential with one lifetime of 2 μs attributed to the intercalative form and a second lifetime of 0.6 μs (indistinguishable from the free species) assigned to the surface-bound form.<sup>6</sup> This enhancement in luminescence, coupled to shape- and symmetry-selective binding, has been useful in probing nucleic acid conformations and in the development of new phototherapeutics.<sup>4,7,8</sup> However, the background luminescence of the free form, the relatively weak binding, and the extent of enhancement on binding appeared insufficient for the broader application of the ruthenium complexes as general nonradioactive nucleic acid probes. Here we report the application of a novel transition-metal complex as a true molecular "light switch" for DNA. This probe is Ru(bpy)<sub>2</sub>(dppz)<sup>2+</sup> (bpy = 2,2'-bipyridine, dppz = dipyrido[3,2-a:2',3'-c]phenazine),<sup>9</sup> which shows no photoluminescence in

Table I. Luminescence<sup>a</sup> of Ru(bpy)<sub>2</sub>(dppz)<sup>2+</sup> in the Absence and Presence of Polynucleotides

solvent	DNA <sup>b</sup>	rel luminescence <sup>c</sup> (steady state)	λ <sub>em</sub> <sup>d</sup> nm	τ, ns
H <sub>2</sub> O		0.0		
50 mM NaCl/5 mM Tris, pH 7.0		0.0		
2-propanol		1.0	622	210
methanol		0.23	610	30
50 mM NaCl/5 mM Tris, pH 7.0	calf thymus	0.61	632	75, 259
50 mM NaCl/5 mM Tris, pH 7.0	poly[d(GC)]	0.72	628	75, 250
50 mM NaCl/5 mM Tris, pH 7.0	poly[r(AU)]	0.09	650	
20 mM NaCl/2 mM Tris, pH 7.0/4 μM Co(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>	Z-poly[d(GC)]	0.79	640	
20 mM NaCl/2 mM Tris, pH 7.0/4 μM Co(NH <sub>3</sub> ) <sub>6</sub> <sup>3+</sup>	calf thymus	0.61	632	

<sup>a</sup> All measurements were conducted at 25 °C with Ru(bpy)<sub>2</sub>(dppz)<sup>2+</sup> at 10 μM. <sup>b</sup> The concentration of DNA used was 100 μM nucleotides. <sup>c</sup> The luminescence spectra were measured by using an SLM 8000C spectrofluorimeter with excitation at 482 nm. Values are given for the maximum intensity found relative to that found in 2-propanol at 622 nm. <sup>d</sup> Wavelength with maximum emission (uncorrected for photomultiplier tube response) upon excitation at 482 nm. <sup>e</sup> Emission lifetimes were determined by deconvolution of biexponential decay traces in single photon counting experiments as described previously.<sup>4</sup> Values given have an estimated uncertainty of 10%.

aqueous solution at ambient temperatures, but displays intense photoluminescence in the presence of double-helical DNA, to which the complex binds avidly.<sup>10</sup>



Ru(bpy)<sub>2</sub>(dppz)<sup>2+</sup> appeared to be a prime candidate for application as a spectroscopic probe for nucleic acids owing to its shape<sup>7</sup> and the sensitivity of its excited-state properties to environment.<sup>9</sup> While the complex does not luminesce in aqueous solution, it shows appreciable solvatochromic luminescence in ethanol (λ<sub>exc</sub> = 482 nm, λ<sub>em</sub> = 610 nm), acetonitrile (λ<sub>exc</sub> = 482 nm, λ<sub>em</sub> = 615 nm) and 2-propanol (λ<sub>exc</sub> = 482 nm, λ<sub>em</sub> = 622 nm) (Table I). Electrochemical and photophysical measurements of Ru(bpy)<sub>2</sub>(dppz)<sup>2+</sup> in its ground and excited states show that the charge transfer is directed from the metal center to the phenazine ring, and the major nonradiative deactivation pathway for the complex likely involves the protonation of the phenazine nitrogen atoms in the excited state.<sup>9</sup> Not surprisingly owing to the extended planar structure of the dppz ligand<sup>7c</sup> and in contrast to Ru(bpy)<sub>3</sub><sup>2+</sup>,<sup>4</sup> Ru(bpy)<sub>2</sub>(dppz)<sup>2+</sup> binds to double-helical DNA by intercalation; topoisomerase assays<sup>11</sup> indicate an unwinding angle of 30 ± 11° per ruthenium bound. Given the preferential charge transfer onto the intercalating dppz ligand, the luminescence of the bound complex therefore provides a sensitive reporter of its helical environment.

(10) The equilibrium binding constant of Ru(bpy)<sub>2</sub>(dppz)<sup>2+</sup> to calf thymus DNA in 50 mM NaCl/5 mM Tris, pH 7.0, at ambient temperatures is >10<sup>6</sup> M<sup>-1</sup> based upon absorption titrations and equilibrium dialysis experiments (A. M. Pyle, data in our laboratory). The complex binds comparably to AT-rich and GC-rich DNAs.

(11) Waring, M. J. *J. Mol. Biol.* 1970, 54, 247. Wang, J. C. *J. Mol. Biol.* 1974, 89, 783. Keller, W. *Proc. Natl. Acad. Sci. U.S.A.* 1975, 72, 4876.

\* To whom correspondence should be addressed at the California Institute of Technology.

<sup>†</sup> California Institute of Technology.

<sup>‡</sup> Université Louis Pasteur.

<sup>§</sup> Columbia University.

(1) Langer-Safer, P. R.; Levine, M.; Ward, D. C. *Proc. Natl. Acad. Sci. U.S.A.* 1982, 79, 4381. Le Pecq, J. B.; Yot, P.; Paoletti, C. C. *Heb. Seances Acad. Sci. R.* 1964, 259, 1786. Ward, D. C.; Horn, T.; Reich, E. *J. Biol. Chem.* 1972, 247, 4014. Sharp, P. A.; Sugden, B.; Sambrook, J. *Biochemistry* 1973, 12, 3055. Menisser, J.; Hunting, D. J.; DeMurcia, G. *Anal. Biochem.* 1985, 148, 339. Matthews, J. A.; Batki, A.; Hynds, C.; Kricka, L. J. *Anal. Biochem.* 1985, 151, 205.

(2) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* 1988, 84, 85.

(3) Barton, J. K.; Danishefsky, A. T.; Goldberg, J. M. *J. Am. Chem. Soc.* 1984, 106, 2172. Barton, J. K.; Basile, L. A.; Danishefsky, A. T.; Alexandrescu, A. *Proc. Natl. Acad. Sci. U.S.A.* 1984, 81, 1961. Mei, H.-Y.; Barton, J. K. *J. Am. Chem. Soc.* 1986, 108, 7414.

(4) Kumar, C. V.; Barton, J. K.; Turro, N. J. *J. Am. Chem. Soc.* 1985, 107, 5518. Barton, J. K.; Goldberg, J. M.; Kumar, C. V.; Turro, N. J. *J. Am. Chem. Soc.* 1986, 108, 2081.

(5) For applications to electron-transfer reactions, see also: Barton, J. K.; Kumar, C. V.; Turro, N. J. *J. Am. Chem. Soc.* 1986, 108, 6391. Purugganan, M. D.; Kumar, C. V.; Turro, N. J.; Barton, J. K. *Science* 1988, 241, 1645.

(6) More recent <sup>1</sup>H NMR experiments further support these assignments. See: Rehmann, J. P.; Barton, J. K. *Biochemistry* 1990, 29, 1701, 1710.

(7) Barton, J. K. *Science* 1986, 233, 727. Fleisher, M. B.; Mei, H.-Y.; Barton, J. K. *Nucleic Acids Mol. Biol.* 1988, 2, 65. Pyle, A. M.; Rehmann, J. P.; Meshoyrer, R.; Kumar, C. V.; Turro, N. J.; Barton, J. K. *J. Am. Chem. Soc.* 1989, 111, 3051.

(8) Kelly, J. M.; Murphy, M. J.; McConnell, D. J.; OhUigin, C. *Nucleic Acids Res.* 1985, 13, 167. Kelly, J. M.; Kelly, J. M.; Tossi, A. B.; McConnell, D. J.; OhUigin, C. *Nucleic Acids Res.* 1985, 13, 6017. Stradowski, C.; Gerner, H.; Currell, L. J.; Schulte-Frohlinde, D. *Biopolymers* 1987, 26, 189. Kelly, J. M.; Van der Putten, W. J. M.; McConnell, D. J. *Photochem. Photobiol.* 1987, 45, 167.

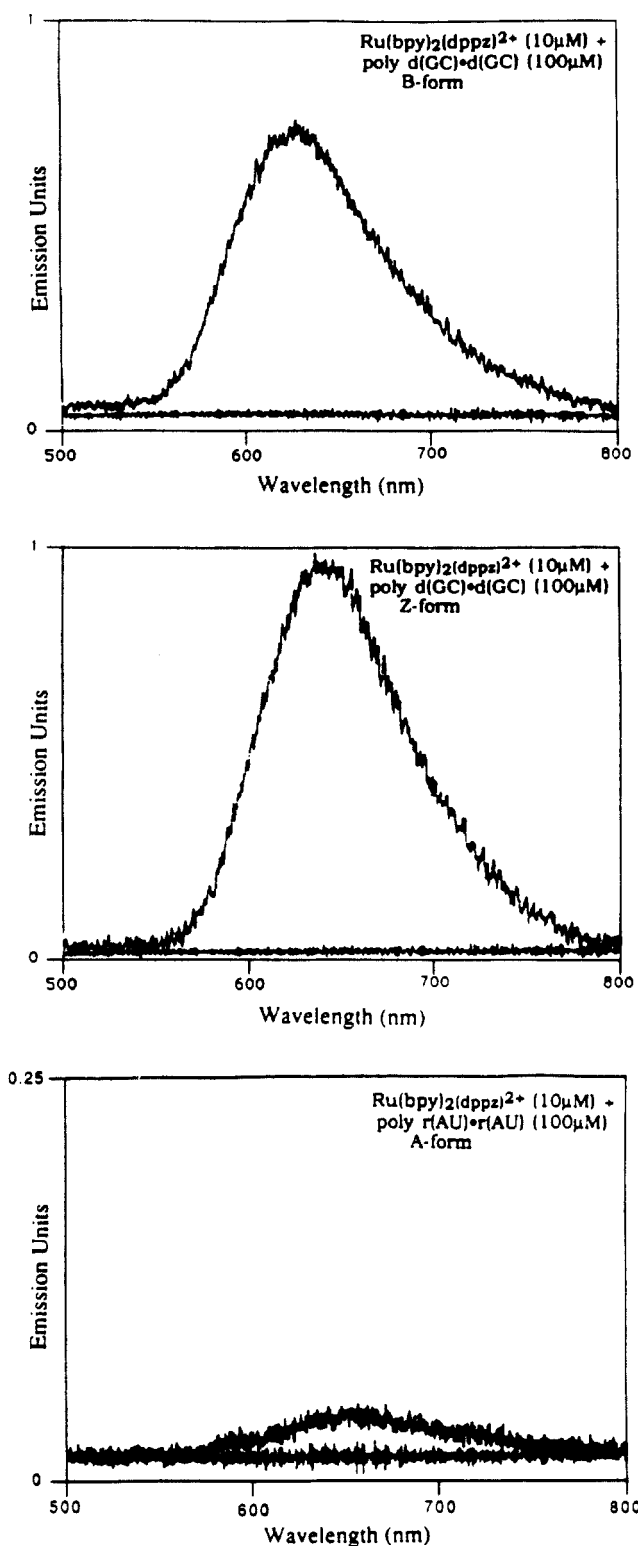
(9) Chambron, J.-C.; Sauvage, J.-P.; Amouyal, E.; Koffi, P. *New J. Chem.* 1985, 9, 527. Amouyal, E.; Homsl, A.; Chambron, J.-C.; Sauvage, J.-P. *J. Chem. Soc., Dalton Trans.*, in press.

Preparations<sup>9,12</sup> of  $\text{Ru}(\text{bpy})_2(\text{dppz})^{2+}$  ( $10\ \mu\text{M}$ ) in buffered aqueous solutions show no detectable luminescence. In the presence of  $100\ \mu\text{M}$  calf thymus DNA, however, luminescence, with emission centered at  $632\ \text{nm}$  and comparable in intensity to that found in 2-propanol (where  $\Phi \geq 0.02$ ),<sup>13</sup> is apparent (Table I). For comparison,  $\Phi(\text{Ru}(\text{bpy})_3^{2+}) = 0.042$  for photoluminescence in aqueous solution,<sup>2</sup> both in the presence of DNA and in its absence; there is no detectable spectroscopic perturbation for  $\text{Ru}(\text{bpy})_3^{2+}$  by DNA under physiological conditions. Single photon counting experiments at  $25\ ^\circ\text{C}$  reveal a biexponential decay of emission from  $\text{Ru}(\text{bpy})_2(\text{dppz})^{2+}$  bound to DNA with a short-lived component of  $75\ \text{ns}$  and a longer lived component of  $259\ \text{ns}$ .<sup>14</sup> As with  $\text{Ru}(\text{phen})_3^{2+}$ ,<sup>4</sup> the anionic solution quencher of the ruthenium complex,  $\text{Fe}(\text{CN})_6^{4-}$ , preferentially quenches the short-lived component; we therefore assign the longer lived component as the less accessible, tightly intercalated form.<sup>15</sup>

The extent of enhancement on DNA binding is perhaps best illustrated in steady-state luminescence experiments (Figure 1). In the presence of  $100\ \mu\text{M}$  poly[d(GC)-d(GC)] (B form), intense emission centered at  $628\ \text{nm}$  is observed, whereas in the absence of polynucleotide, no emission is detectable. We estimate from our limits of detection the enhancement factor upon binding to DNA to be  $>10^4$ . Similar results are evident with Z-form poly[d(GC)-d(GC)]; here the relative intensity is still greater and the emission maximum is shifted to  $640\ \text{nm}$ .<sup>16</sup> Interestingly, only weak emission ( $\lambda_{\text{em}} = 650\ \text{nm}$ ) is apparent in the presence of poly[r(AU)-r(AU)], an A-form helical polymer. Given that  $\text{Ru}(\text{phen})_3^{2+}$  does not appear to intercalate into synthetic double-stranded RNA (there is no long-lived luminescent component in emission, for example),<sup>4</sup> these results suggest that it may be the tightly intercalated interaction that is primarily responsible for preserving emission in the dppz complex.

These results point also to the selective nature of  $\text{Ru}(\text{bpy})_2(\text{dppz})^{2+}$  as a molecular switch, responding sensitively to the subtle changes in the structure of the helix. As can be seen in Table I, variations as a function of DNA substrate are detected not only in the intensity of photoluminescence but also in the emission maximum. With B-form polymers, poly[d(GC)-d(GC)] and mixed-sequence calf-thymus DNA show emission maxima at  $628$  and  $632\ \text{nm}$ , respectively; with the Z- and A-form helices, the maximum shifts to still longer wavelengths ( $640$  and  $650\ \text{nm}$  for the Z- and A-form polymers, respectively). It is not clear whether it is the electronic character of the DNA bases and its overlap with the phenazine ring, the accessibility of the phenazine ring to protonation, or some mixture thereof that is responsible for the novel luminescent properties associated with the interaction with the helix.

In summary, we find  $\text{Ru}(\text{bpy})_2(\text{dppz})^{2+}$  to be a highly sensitive spectroscopic reporter of double-helical DNA. In aqueous solution, luminescence is detectable only when  $\text{Ru}(\text{bpy})_2(\text{dppz})^{2+}$  has intercalated in (or is perhaps otherwise shielded by) the nucleic acid structure. The emission characteristics furthermore sensitively distinguish both in terms of intensity and emission maximum the different helical forms of the polynucleotide. We therefore conclude that  $\text{Ru}(\text{bpy})_2(\text{dppz})^{2+}$  can serve as a true molecular "light switch" for DNA structures, and tethered onto oligonucleotides,<sup>18</sup> the complex may be useful as a sensitive, nonra-



**Figure 1.** Steady-state emission spectra of  $\text{Ru}(\text{bpy})_2(\text{dppz})^{2+}$  ( $10\ \mu\text{M}$ ) in the absence and presence of B-form (top), Z-form (middle), and A-form (bottom) double-helical nucleic acids. In each case in the absence of polynucleotide, only the base-line spectrum, the same level of emission as detected with pure solvent, is obtained for the ruthenium complex in  $50\ \text{mM}\ \text{NaCl}/5\ \text{mM}\ \text{Tris}$ , pH 7.0, at  $25\ ^\circ\text{C}$ . In the presence of B-DNA,  $100\ \mu\text{M}$  poly[d(GC)-d(GC)] has been added. For the spectrum in the presence of Z-DNA,  $100\ \mu\text{M}$  poly[d(GC)-d(GC)] has also been added, but the buffer (both in the presence and in the absence of DNA) contains instead  $20\ \text{mM}\ \text{NaCl}/2.0\ \text{mM}\ \text{Tris}/4\ \mu\text{M}\ \text{Co}(\text{NH}_3)_6^{3+}$ , pH 7.0, to promote Z formation. For the spectra of  $\text{Ru}(\text{bpy})_2(\text{dppz})^{2+}$  ( $10\ \mu\text{M}$ ) taken in the absence (base line) and presence of A-form poly[r(AU)-r(AU)] ( $100\ \mu\text{M}$ ), the buffer employed is again  $50\ \text{mM}\ \text{NaCl}/5.0\ \text{mM}\ \text{Tris}$ , pH 7.0. Note that for the A-form panel, higher sensitivity ( $4\times$ ) was employed to record both spectra.

(12) For ligand synthesis, see also: Dickeson, J. E.; Summers, L. A. *Aust. J. Chem.* **1970**, *23*, 1023.

(13) This quantum yield for photoluminescence is based upon comparison to that of  $\text{Ru}(\text{bpy})_3^{2+}$  in aqueous solution.<sup>2</sup>

(14) The  $259\text{-ns}$  component accounted for 66% of the emission.

(15) The short-lived component may correspond, as with  $\text{Ru}(\text{phen})_3^{2+}$ ,<sup>4</sup> to a surface-bound mode in the minor groove or to an alternate binding mode in which the dppz ligand is less shielded than if tightly intercalated.

(16) Unlike other DNA-intercalating species such as ethidium,<sup>17</sup>  $\text{Ru}(\text{bpy})_2(\text{dppz})^{2+}$  does not promote a Z-B transition, as the spectral differences seen here support. See: Friedman, A. E.; Kumar, C. V.; Turro, N. J.; Barton, J. K., to be submitted.

(17) Pohl, F. M.; Jovin, T. M.; Baehr, W.; Holbrook, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1972**, *69*, 3805-9.

(18) Bannwarth, W.; Schmidt, D.; Stallard, R. I.; Hornung, C.; Knorr, R.; Müller, F. *Helv. Chim. Acta* **1988**, *71*, 2085. Telser, J.; Cruickshank, K. A.; Schanze, K. S.; Netzel, T. L. *J. Am. Chem. Soc.* **1989**, *111*, 7221.

dioactive, luminescent DNA probe in both heterogeneous and homogeneous assays.

**Acknowledgment.** We are grateful to the NIH (GM33309 to J.K.B. and NRSA Fellowship CA08518 to A.E.F.), the NSF (CHE85-13521 to N.J.T.), the AFOSR (88-0043 to N.J.T.), and the CNRS (to J.-C.C. and J.-P.S.) for their financial support of this research.

# **Synthesis and Characterization of the First Example of a Metallocarborane That Incorporates an Alkaline-Earth Metal: The Molecular Structure of *clos*-1,1,1,1-(MeCN)<sub>4</sub>-1,2,4-CaC<sub>2</sub>B<sub>10</sub>H<sub>12</sub><sup>1</sup>**

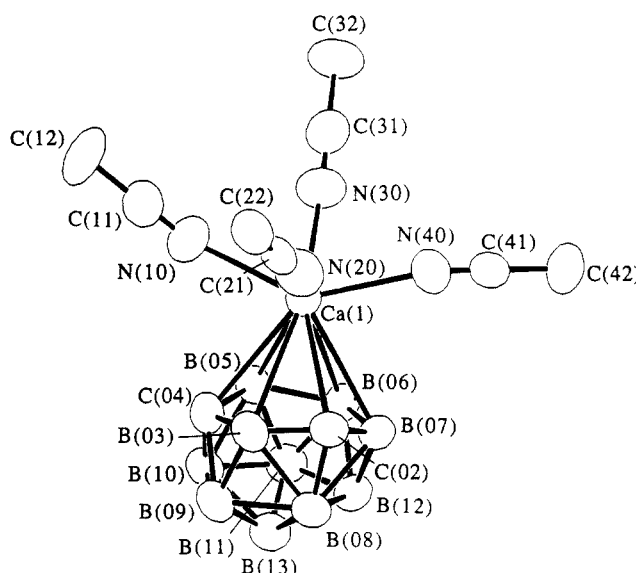
Rajesh Khattar, Carolyn B. Knobler, and  
M. Frederick Hawthorne\*

Department of Chemistry and Biochemistry  
University of California at Los Angeles  
Los Angeles, California 90024

Received January 24, 1990

The organometallic chemistry of the alkaline-earth metals has received particular attention in recent years.<sup>2-10</sup> In this context, high yield synthesis routes to the cyclopentadienyl<sup>2-8</sup> and cyclooctatetraenediyl<sup>10</sup> complexes of calcium, strontium, and barium have been developed and the molecular structures of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ba,<sup>6</sup> (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ca,<sup>2</sup> [(C<sub>5</sub>Me<sub>5</sub>)Ca(μ-I)(THF)<sub>2</sub>]<sub>2</sub>,<sup>9</sup> and [C<sub>5</sub>H<sub>5</sub>-1,3-(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>M(THF)<sup>8</sup> (M = Ca or Sr) have been established crystallographically. The desolvated species possess polymeric structures in the solid state [for example, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ba<sup>6</sup> and (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ca<sup>2</sup>], are monomeric in the gas phase [for example, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>M (M = Ca,<sup>3,5</sup> Sr,<sup>11</sup> or Ba<sup>11</sup>)], and the solvated species are either dimeric or monomeric in the solid state.<sup>8,9</sup> However, there is no previous report of a discrete metallocarborane cluster that incorporates an alkaline-earth metal. We here report the high-yield synthesis and characterization of such a metallocarborane as well as the molecular structure of the novel calcium carborane complex, *clos*-1,1,1,1-(MeCN)<sub>4</sub>-1,2,4-CaC<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, the first structurally authenticated example of an alkaline-earth metallocarborane.

The addition of THF solutions of Na<sub>2</sub>[*nido*-7,9-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>]<sup>12</sup> to THF solutions of CaI<sub>2</sub> at room temperature over a period of 0.5 h affords a colorless complex, which is insoluble in THF but soluble in other coordinating solvents such as MeCN or DMF. Recrystallization of this complex from MeCN/Et<sub>2</sub>O produces colorless needle-like crystals; the X-ray study showed it to have



**Figure 1.** The molecular structure of *clos*-1,1,1,1-(MeCN)<sub>4</sub>-1,2,4-CaC<sub>2</sub>B<sub>10</sub>H<sub>12</sub> (1). All hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): Ca(1)–N(10), 2.471 (5); Ca(1)–N(20), 2.431 (5); Ca(1)–N(30), 2.476 (5); Ca(1)–N(40), 2.508 (5); Ca(1)–C(2), 2.701 (5); Ca(1)–B(3), 2.879 (6); Ca(1)–C(4), 2.895 (5); Ca(1)–B(5), 2.649 (6); Ca(1)–B(6), 2.828 (6); Ca(1)–B(7), 2.935 (6); C(2)–B(3), 1.518 (7); C(2)–B(7), 1.515 (7); C(2)–B(8), 1.734 (7); C(2)–B(9), 2.789 (7); C(2)–B(12), 2.814 (8); C(4)–B(3), 1.638 (8); C(4)–B(5), 1.701 (7); C(4)–B(9), 1.692 (8); C(4)–B(10), 1.691 (7); B(3)–B(8), 2.037 (9); B(3)–B(9), 1.840 (8); B(3)–B(10), 2.935 (8); B(5)–B(6), 1.739 (7).

the formulation Ca(C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>)(MeCN)<sub>4</sub> (1).<sup>13</sup> The complex 1 is extremely air- and moisture-sensitive. The presence of the [*nido*-7,9-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>]<sup>2-</sup> fragment in the complex 1 is supported by the fact that the known [*nido*-9,12-C<sub>2</sub>B<sub>10</sub>H<sub>13</sub>]<sup>-</sup> (<sup>1</sup>H and <sup>11</sup>B NMR, vide infra) is produced upon exposure to moisture/H<sub>2</sub>O.<sup>14-16</sup> Complex 1 serves as a source of [*nido*-7,9-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>]<sup>2-</sup> by its reaction with YbI<sub>2</sub>(MeCN)<sub>2</sub> in MeCN to afford the known<sup>17</sup> *clos*-1,1,1,1-(MeCN)<sub>4</sub>-1,2,4-YbC<sub>2</sub>B<sub>10</sub>H<sub>12</sub> in quantitative yield.

The molecular structure<sup>18</sup> of 1 is illustrated in Figure 1, along with selected interatomic distances. The calcium atom asymmetrically caps the open puckered hexagonal face of the [*nido*-7,9-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>]<sup>2-</sup> ligand. Four acetonitrile ligands are bonded to the calcium atom. The Ca–N bond distances range from 2.43 to 2.51 Å, and calcium–carborane distances fall in the range 2.65–2.94 Å. The Ca(1)–C(2) distance of 2.70 Å compares very well with that reported for the complexes [C<sub>5</sub>H<sub>5</sub>-1,3-

(1) Numbers accompanying formulas refer to the positions of the heteroatoms within the *clos*-metallocarborane framework and to the location of the exopolyhedral substituents. Lowest numbers consistent with the molecular geometry are given to carbon in accordance with the inverse periodic order adhered to by the IUPAC Inorganic Nomenclature Committee (see: Adams, R. M. *Pure Appl. Chem.* 1972, 30, 683). The numbering system used for the *nido*-carborane anions described herein is identical with that previously employed (see: Dustin, D. F.; Dunks, G. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1973, 95, 1109).

(2) Zerger, R.; Stucky, G. *J. Organomet. Chem.* 1974, 80, 7.

(3) Andersen, R. A.; Boncella, J. M.; Burns, C. J.; Blom, R.; Haaland, A.; Volden, H. V. *J. Organomet. Chem.* 1986, 312, C49.

(4) Burns, C. J.; Andersen, R. A. *J. Organomet. Chem.* 1987, 325, 31.

(5) Andersen, R. A.; Blom, R.; Boncella, J. M.; Burns, C. J.; Volden, H. V. *Acta Chem. Scand., Ser. A* 1987, A41, 24.

(6) Hanusa, T. P.; Williams, R. A.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* 1988, 1045.

(7) McCormick, M. J.; Williams, R. A.; Levine, L. J.; Hanusa, T. P. *Polyhedron* 1988, 7, 725.

(8) Engelhardt, L. M.; Junk, P. C.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* 1988, 1500.

(9) McCormick, M. J.; Sockwell, S. C.; Davies, C. E. H.; Hanusa, T. P.; Huffman, J. C. *Organometallics* 1989, 8, 2044.

(10) Hutchings, D. S.; Junk, P. C.; Patalinghug, W. C.; Raston, C. J.; White, A. H. *J. Chem. Soc., Chem. Commun.* 1989, 973.

(11) Andersen, R. A.; Blom, R.; Burns, C. J.; Volden, H. V. *J. Chem. Soc., Chem. Commun.* 1987, 768.

(12) Salentine, C. G.; Hawthorne, M. F. *Inorg. Chem.* 1976, 15, 2872.

(13) Data for 1: IR (Nujol mull, NaCl)  $\nu_{\text{B-H}}$  2466 (s), 2419 (s, br),  $\nu_{\text{MeCN}}$  2302 (m), 2273 (s) cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>CN, 20 °C, ppm) 4.12 (s, br, carboranyl C–H); <sup>11</sup>B NMR (in MeCN, 20 °C; chemical shifts referenced to external BF<sub>3</sub>·OEt<sub>2</sub>; peaks upfield of the reference are designated as negative; areas given in parentheses) 2.2 (4), <sup>1</sup>J<sub>BH</sub> = 103 Hz, –6.4 (3), <sup>1</sup>J<sub>BH</sub> = 147 Hz, –17.6 (3), <sup>1</sup>J<sub>BH</sub> = 130 Hz. Anal. Calcd for C<sub>10</sub>H<sub>24</sub>B<sub>10</sub>N<sub>4</sub>Ca: C, 34.48; H, 6.89; N, 16.09. Found: C, 30.09; H, 7.38; N, 13.30. These values are better suited to C<sub>8</sub>H<sub>21</sub>B<sub>10</sub>N<sub>3</sub>Ca, which contains one less MeCN per molecule. Calcd for C<sub>8</sub>H<sub>21</sub>B<sub>10</sub>N<sub>3</sub>Ca: C, 31.27; H, 6.84; N, 13.68. We have not been able to obtain satisfactory elemental analyses of 1 due to facile loss of a MeCN ligand during analytical sample preparation. Loss of coordinated solvent molecules from organoalkaline-earth metal complexes is common (refs 3, 4, and 6).

(14) Dunks, G. B.; Wiersema, R. J.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* 1972, 899.

(15) Tolpin, E. I.; Lipscomb, W. N. *Inorg. Chem.* 1973, 12, 2257.

(16) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* 1973, 12, 2674.

(17) Manning, M. J. Ph.D. Dissertation, University of California at Los Angeles, Los Angeles, 1988.

(18) Crystal data: C<sub>10</sub>H<sub>24</sub>B<sub>10</sub>N<sub>4</sub>Ca, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 8.6985 (7) Å, *b* = 15.825 (1) Å, and *c* = 15.423 (2) Å,  $\beta$  = 90.106 (3)°, *V* = 2123 Å<sup>3</sup>, *Z* = 4,  $\mu$ (Cu K $\alpha$ ) = 25.1 cm<sup>-1</sup>, *D*(calcd) = 1.05 g cm<sup>-3</sup>, *T* = 298 K,  $\lambda$  = 1.5418 Å, colorless needle specimen, 0.15 × 0.25 × 0.65 mm. A crystal obtained from MeCN/Et<sub>2</sub>O solution was sealed in a capillary on a modified Syntex P1 diffractometer. Data were collected at 298 K in the  $\theta$ –2 $\theta$  scan mode. Of the 2177 unique reflections measured, 1676 were considered observed (*I* > 3 $\sigma$ (*I*)) and were used in the subsequent structure analysis. The final discrepancy index was *R* = 0.050, *R*<sub>w</sub> = 0.070, GOF = 2.55;  $\Delta(\rho)$  = 0.2 e Å<sup>-3</sup>.