[13] Hexastyrylbenzene and substituted hexastyrylbenzenes were prepared starting from the threefold coupling product of 1,3,5-tribromo-2,4,6-trimethylbenzene and styrene: H. Meier, N. Hanold, H. Kalbitz, *Synthesis* **1997**, 276.

[14] H. C. Brown, S. K. Gupta, *J. Am. Chem. Soc.* **1972**, *94*, 4370-4371.

[15] W. A. Hermann, C. Broßmer, K. Öfele, C.-P. Reisinger, T. Priermeier, M. Beller, H. Fischer, *Angew. Chem.* **1995**, *107*, 1989-1992; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1844-1848.

[16] T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi, K. Hirotsu, *J. Am. Chem. Soc.* **1984**, *106*, 158-163.

[17] R. F. Cunico, F. J. Clayton, *J. Org. Chem.* **1976**, *41*, 1480-1482.

[18] Good-quality crystals of **3a** and **3d** were obtained by letting ethanol slowly diffuse into a saturated solution of **3a** in hexane and **3d** in hexane/ethanol.

[19] Crystal structure analyses: **3a**: Nicolet R3m/V four-circle diffractometer, $Mo_{K\alpha}$ (graphite monochromator, $\lambda = 0.71069$ Å), $T = 125$ K; crystal dimensions $0.52 \times 0.31 \times 0.45$ mm^3; $C_{42}H_{66}$, $M_r = 570.99$; $a = 10.691(3)$, $b = 14.697(3)$, $c = 14.714(4)$ Å, $\alpha = 60.29(2)$, $\beta = 77.78(2)$, $\gamma = 73.35(2)^\circ$, $V = 1917.2(8)$ Å^3; triclinic, space group $P\bar{1}$, $Z = 2$, $\rho_{calcd} = 0.98$ g cm^{-3}, $\mu = 0.05$ mm^{-1}; 5015 independent reflections with $3 \leq 2\theta \leq 45^\circ$, 3872 observed with $F_0 \leq 4\sigma(F)$; $R(F) = 0.0491$, $R_w(F) = 0.0573$ [20]. **3d**: STOE-AED2 diffractometer, $Mo_{K\alpha}$ ($\lambda = 0.71069$ Å), $T = 153$ K; crystal dimensions $0.4 \times 0.2 \times 0.2$ mm^3; $C_{36}H_{66}Si_6$, $M_r = 667.43$; $a = 13.288(6)$, $b = 14.039(6)$, $c = 14.760(6)$ Å, $\alpha = 66.44(3)$, $\beta = 67.88(3)$, $\gamma = 68.95(3)^\circ$, $V = 2267(2)$ Å^3, triclinic, space group $P\bar{1}$, $Z = 2$, $\rho_{calcd} = 0.978$ g cm^{-3}, $\mu = 0.204$ mm^{-1}; 7959 independent reflections with $7 \leq 2\theta \leq 50^\circ$; 5811 observed with $F_0 \leq 4\sigma(F)$; $R(F) = 0.0616$, $R_w(F) = 0.1436$ [20]. **7**: STOE-AED2 diffractometer, $Mo_{K\alpha}$ ($\lambda = 0.71069$ Å), $T = 153$ K; crystal dimensions $0.6 \times 0.6 \times 0.5$ mm^3; $C_{42}H_{78}$, $M_r = 583.04$; $a = 23.819(3)$, $b = 23.819(3)$, $c = 6.1908(12)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 120^\circ$; $V = 3041.8(9)$ Å^3; rhombohedral, space group $R\bar{3}$, $Z = 3$, $\rho_{calcd} = 0.955$ g cm^{-3}, $\mu = 0.052$ mm^{-1}; 894 independent reflections with $7 \leq 2\theta \leq 45^\circ$; 695 observed with $F_0 \leq 4\sigma(F)$; $R(F) = 0.0450$, $R_w(F) = 0.1040$ [20]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-100015 and -100016. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).

[20] SHELXTL-PLUS (Program System for Crystal Structure Solution and Refinement, Universität Göttingen).

[21] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441-451.

[22] W. R. Roth, Universität Bochum (Germany), personal communication. We are indebted to Professor Roth for carrying out the calculations with his MM2-ERW program.

[23] J. M. Bollinger, J. J. Burke, E. M. Arnett, *J. Org. Chem.* **1966**, *31*, 1310.

[24] The cyclic voltammogram was kindly measured by Prof. Dr. S. Bäuerle and Dipl.-Chem. M. Emge, Universität Ulm (Germany)

[25] J. O. Howell, J. M. Goncalves, C. Amatore, L. Klansinc, R. M. Wightman, J. K. Kochi, *J. Am. Chem. Soc.* **1984**, *106*, 3968-3976.

First Structural Characterization of a Benzophenone Ketyl Complex[**]

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Although the formation of ketyls by one-electron reduction of ketones has been known for more than a hundred years,[1, 2] structurally characterized examples of this important class of highly reactive species remain very rare and are still limited solely to the fluorenone ketyl species that were recently isolated in our laboratories.[3] Isolation and structural characterization of new ketyl complexes continue to be of great importance and interest. Benzophenone ketyl is among the best known and most widely used ketyls.[1, 2, 4] Previous attempts to isolate a benzophenone ketyl species by utilization of low-valent titanium and lanthanide reducing agents were not successful.[4-6] Reaction of [$CpTiCl_2$] with benzophenone in THF/ether was reported to give rapidly the corresponding pinacol-coupling product.[6] The use of a sterically demanding titanium(III) reductant such as [$Ti(OSi\textit{t}Bu_3)_3$] suppressed the pinacol-coupling reaction, but benzophenone dimerized by coupling of the *para*-carbon atom of a phenyl group with the carbonyl carbon of another molecule.[5f] Reactions of benzophenone with sterically demanding lanthanide reducing agents such as [$Ln(OAr_2(L)_n$] (Ln = Sm, Yb; Ar = 2,6-$\textit{t}Bu_2$-4-MeC_6H_2); L = thf, hmpa),[3a, b] [R_2Sm] (R = BH(3,5-dimethylpyrazolyl)$_3$),[7] or Ln/hmpa[3d] did not afford structurally characterizable benzophenone ketyl species either, but resulted in hydrogen abstraction in some cases, although many of these reducing agents have been successfully used for the isolation of fluorenone ketyl complexes.[3] All these results show that benzophenone ketyl species are extremely reactive and much more unstable than the corresponding fluorenone ketyl species. After the survey of several different types of reducing agents, we successfully isolated structurally characterizable benzophenone ketyl species by binding them to a calcium(II) ion containing hmpa ligands. In this communication, we report the isolation and structural characterization of a bis(benzophenone ketyl)calcium complex, which constitutes the first structurally characterized benzophenone ketyl complex, as well as the first structurally characterized complex of an alkaline earth metal with a ketyl.[8, 9] Its reaction with 2-propanol is also described.

In the presence of three equivalents of hexamethylphosphoric triamide (HMPA), reaction of fresh calcium chips with two equivalents of benzophenone in THF gradually gave a blue solution, which after filtration, concentration, and addition of hexane, afforded blue blocks of **1** in 77% yield of isolated product (Scheme 1). The UV/Vis ($\lambda = 635$ nm, $\varepsilon = 3.8 \times 10^3$ M^{-1}cm^{-1})[5c] and ESR ($g = 2.0028$) spectra of **1** in THF are very similar to those reported for the benzophenone ketyl species generated in situ.[5]

An X-ray analysis has shown that **1** is a bis(benzophenone ketyl)calcium(II) complex, which possesses a distorted trigonal-bipyramidal structure with one hmpa and two ketyl ligands in equatorial and two hmpa ligands in apical positions (Figure 1).[10] The two ketyl ligands form an O-Ca-O angle of 114.2(4)°, and the distance between the two radical carbon atoms (C(1) and C(14)) is 5.99 Å. The overall structure of **1** is similar to that of the calcium(II) aryloxide complex [$Ca(OAr)_2(thf)_3$] (Ar = 2,6-$\textit{t}Bu_2$-4-MeC_6H_2).[11] The bond lengths of the Ca–O(ketyl) bonds in **1** (av 2.20(1) Å) are also similar to those of the Ca–OAr bonds in [$Ca(OAr)_2(thf)_3$] (av 2.206(6) Å).[11, 12] The C–O bonds of the benzophenone ketyl ligands in **1** are significantly longer (av 1.31(2) Å) than that of free benzophenone (1.23(1) Å),[13] but comparable with those of fluorenone ketyls (1.27–1.31 Å).[3] As in fluorenone ketyls, the radical carbon atoms C(1) and C(14) in **1** are nearly coplanar with the atoms around them (d_{max} from the best least-squares plane smaller than 0.03 Å) and are still sp^2-hybridized. However, the planes defined by O(1)-C(1)-C(2)-C(8) and O(2)-C(14)-C(15)-C(21) are not coplanar with any of the phenyl rings. The dihedral angles formed by the O(1)-C(1)-C(2)-C(8) plane and the C(2)–C(7) and C(8)–C(13) phenyl rings are 16° and 30°, respectively, and those formed by the O(2)-C(14)-C(15)-C(21) plane and the C(15)–C(20) and C(21)–C(26) phenyl rings are 20° and 30°, respectively. This is in sharp contrast to fluorenone ketyl in which all the atoms lie in the same plane.[3] The lack of planarity in the whole benzophenone ketyl

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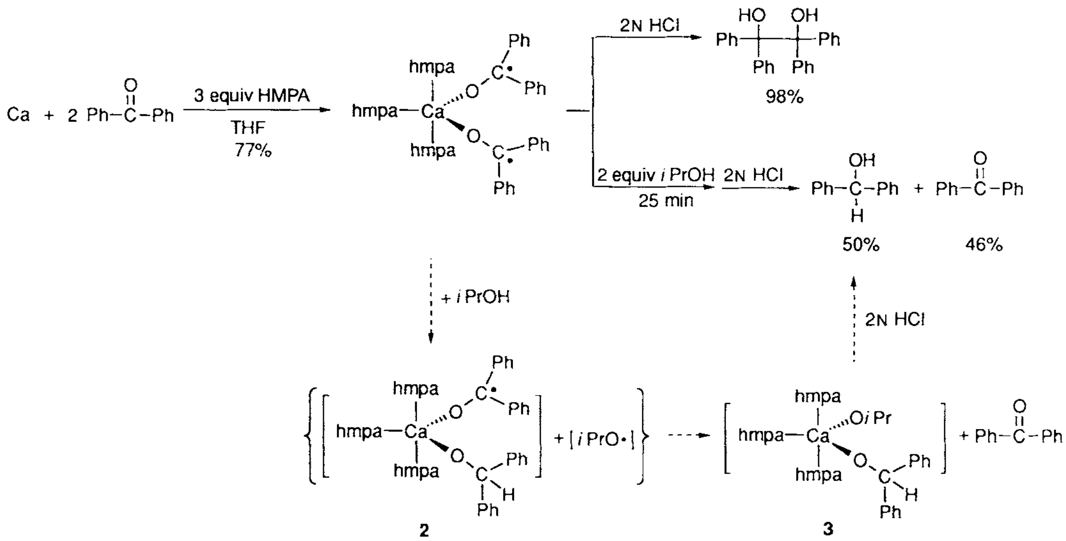

Scheme 1. Synthesis of **1** and mechanism of its reaction with 2-propanol.

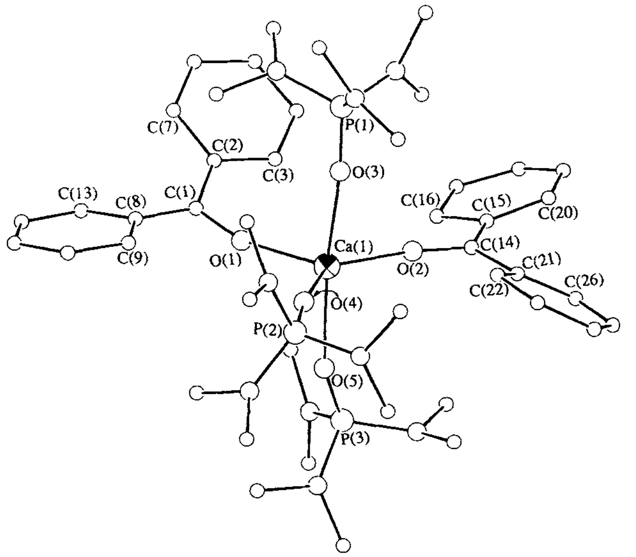

Figure 1. X-ray structure of **1**. Selected bond lengths (Å) and angles (°): Ca(1)–O(1) 2.187(9), Ca(1)–O(2) 2.206(10), Ca(1)–O(3) 2.315(9), Ca(1)–O(4) 2.286(8), Ca(1)–O(5) 2.314(10), O(1)–C(1) 1.31(1), O(2)–C(14) 1.31(2); O(1)-Ca(1)-O(2) 114.2(4), O(1)-Ca(1)-O(3) 95.0(4), O(1)-Ca(1)-O(4), 110.2(4), O(1)-Ca(1)-O(5) 94.5(4), O(2)-Ca(1)-O(3) 89.4(4), O(2)-Ca(1)-O(4) 135.6(4), O(2)-Ca(1)-O(5) 90.0(4), O(3)-Ca(1)-O(4) 86.2(3), O(3)-Ca(1)-O(5) 169.8(4), O(4)-Ca(1)-O(5) 87.1(4), Ca(1)-O(1)-C(1) 162.5(8), Ca(1)-O(2)-C(14) 160.0(10).

unit makes it difficult to stabilize the radical through $p_z-\pi$ orbital interactions with the phenyl groups, and thus explains why benzophenone ketyl is much more reactive than fluorenone ketyl.

Hydrolysis of **1** gave the coupling product, benzopinacol, almost quantitatively (Scheme 1). However, reaction of **1** with two equivalents of 2-propanol in THF followed by hydrolysis afforded benzhydrol and benzophenone in 50% and 46% yields, respectively (Scheme 1). This reaction could be explained by the mechanism shown in Scheme 1. Hydrogen radical abstraction by one of the two ketyls in **1** from 2-propanol[14] gives the ketyl/diphenylmethoxide **2** and the radical *i*PrO•. The subsequent rapid oxidation of the ketyl **2** by the inner-sphere radical *i*PrO• affords benzophenone and **3**, which yields benzhydrol after hydrolysis.

Experimental Section

Typical procedure for the synthesis of **1**: Under argon atmosphere, calcium chips (28 mg, 0.7 mmol) were stirred with CH_2I_2 (2 mol%) in THF (1 mL) for 2 h to activate the metal surface. Hexamethylphosphoric triamide (hmpa; 0.36 mL, 2.1 mmol) was then added by syringe. Addition of a THF solution of benzophenone (255 mg, 1.4 mmol) yielded a blue mixture within a few minutes. After being stirred at room temperature overnight, the blue solution was filtered and concentrated under reduced pressure. Addition of hexane precipitated the benzophenone ketyl complex **1** as blue blocks (510 mg, 0.54 mmol, 77% yield). Anal. calcd for $C_{44}H_{74}N_9O_5P_3Ca$: C 56.09, H 7.92, N 13.38; found: C 55.81, H 8.03, N 13.33.

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[1] For early examples of the formation of ketyl species, see a) F. Bechman, T. Paul, *Justus Ann. Chem.* **1891**, *266*, 1; b) W. Schlenk, T. Weichel, *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 1182; c) W. Schlenk, A. Thal, *ibid.* **1913**, *46*, 2840.

[2] For reviews on metal ketyl mediated organic synthesis, see a) A. Fürstner, B. Bogdanovic, *Angew. Chem.* **1996**, *108*, 2582; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2442; b) T. Wirth, *ibid.* **1996**, *35*, 61 and **1996**, *108*, 65; c) J. W. Huffman in *Comprehensive Organic Synthesis, Vol. 8* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, p. 104; d) G. M. Robertson in *Comprehensive Organic Synthesis, Vol. 3* (Eds. B. M. Trost, I. Fleming, G. Pattenden), Pergamon, Oxford, **1991**, p. 563; e) J. E. McMurry, *Chem. Rev.* **1989**, *89*, 1513; f) B. E. Kahn, R. T. Riecke, *ibid.* **1988**, *88*, 733; g) S. K. Pradhan, *Tetrahedron* **1986**, *42*, 6351; h) J. W. Huffman, *Acc. Chem. Res.* **1983**, *16*, 399; i) J. E. McMurry, *ibid.* **1983**, *16*, 405; *ibid.* **1974**, *7*, 281; j) H. O. House, *Modern Synthetic Reactions*, 2nd ed., W. A. Benjamin, Menlo Park, CA, **1972**, p. 145.

[3] a) Z. Hou, T. Miyano, H. Yamazaki, Y. Wakatsuki, *J. Am. Chem. Soc.* **1995**, *117*, 4421; b) Z. Hou, Y. Wakatsuki, *J. Synth. Org. Chem. Jpn.* **1995**, *53*, 906; c) Z. Hou, A. Fujita, H. Yamazaki, Y. Wakatsuki, *J. Am. Chem. Soc.* **1996**, *118*, 2503; d) *ibid.* **1996**, *118*, 7843; e) Z. Hou, Y. Wakatsuki, *Chem. Eur. J.* **1997**, *3*, 1005.

[4] For example, sodium benzophenone ketyl has been used by almost every chemist in the dehydration and deoxygenation of etheral solvents.

[5] For examples of spectroscopic studies on benzophenone ketyl species, see a) P. H. Rieger, G. K. Fraenkel, *J. Chem. Phys.* **1962**, *37*, 2811; b) P. B. Ayscough, R. Wilson, *J. Chem. Soc.* **1963**, 5412; c) N. Hirota, S. I. Weissman, *J. Am. Chem. Soc.* **1964**, *86*, 2538; d) N. Hirota, *ibid.* **1967**, *89*, 32; e) R. Dams, M. Malinowski, I. Westdorp, H. Y. Geise, *J. Org. Chem.* **1982**, *47*, 248; f) K. J. Covert, P. T. Wolczanski, S. A. Hill, P. J. Krusic, *Inorg. Chem.* **1992**, *31*, 66.

[6] R. S. P. Coutts, P. C. Wailes, R. L. Martin, *J. Organomet. Chem.* **1971**, *50*, 145.

[7] J. Takats, *J. Alloys Compnds.* in press.

[8] Only the structures of sodium and samarium ketyl complexes have been reported [3].

[9] For examples of spectroscopic studies on alkaline earth metal ketyl species, see a) S. W. Mao, N. Hirota, *Chem. Phys. Lett.* **1973**, *22*, 26; b) S. W. Mao, K. Nakamura, N. Hirota, *J. Am. Chem. Soc.* **1974**, *96*, 5341; see also ref. [5c].

[10] Crystal structure data of **1**: $C_{44}H_{74}N_9O_5P_3Ca$, $M_r = 942.14$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.953(2)$, $b = 11.812(2)$, $c = 22.360(5)$ Å, $\alpha = 93.09(2)$, $\beta = 93.36(2)$, $\gamma = 108.90(2)$ Å, $V = 2724(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.15\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo_{K\alpha}}) = 2.432\ \mathrm{cm^{-1}}$, 10383 measured reflections, of which 9566 independent ($R_{int} = 0.06$), empirical absorption correction (max.: 0.997, min.: 0.896), $R = 0.0867$ ($R_w = 0.890$) for 3929 reflections with $I > 2\sigma(I)$ and 559 refined on $|F|$, max. residual electron density: 0.66. The crystal was sealed in a thin-walled glass capillary under N_2. Data were collected on a Mac Science MXC3K diffractometer (20 °C, $\mathrm{Mo_{K\alpha}}$ radiation, graphite monochromator, $\lambda = 0.71073$ Å, ω-2θ mode, $1.5 \leq \theta \leq 27.5°$) and were corrected for Lorentzian and polarization effects. The structure was solved by direct methods with SIR92 in the CRYSTAN-GM software package. Refinements were performed anisotropically for all non-hydrogen atoms by the block-diagonal least-squares method. Attempts to locate the hydrogen atoms were not made. The function minimized in the least-squares refinements was $(\sum(|F_o| - |F_c|)^2$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100217. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).

[11] P. B. Hitchcock, M. F. Lappert, G. A. Lawless, B. Royo, *J. Chem. Soc. Chem. Commun.* **1990**, 1141.

[12] The similarity in length between M–O(fluorenone ketyl) bonds and M–OAr bonds was previously observed; see ref. [3].

[13] E. B. Fleischer, N. Sung, S. Hawkinson, *J. Phys. Chem.* **1968**, *72*, 4311.

[14] Abstraction of a hydrogen atom from an alcohol by a fluorenone ketyl was previously observed; see ref. [3d].

Multicomponent Self-Assembly: Generation and Crystal Structure of a Trimetallic [4]Pseudorotaxane

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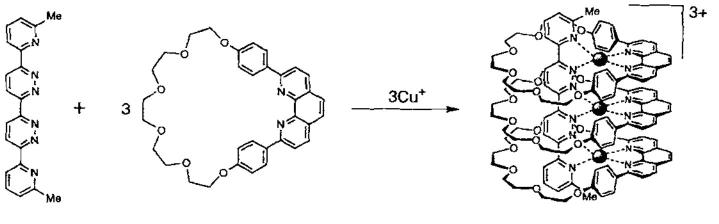
The generation of threaded molecular entities such as pseudorotaxanes, rotaxanes, and catenanes is currently the subject of considerable interest owing to the intriguing synthetic and structural issues posed by such systems.[1, 2] Recent developments in this field include potential applications for materials science and the design of supramolecular devices[3] such as novel polymer composites[4] and simple mechanical molecular processes.[5] In the case of rotaxanes initial synthetic strategies focused on statistical methods of preparation, but more recently supramolecular approaches utilizing intermolecular interactions—such as aromatic attractive forces,[2, 6] hydrogen bonding,[7] and metal ion coordination[2, 8]—have been found to be most efficient for threaded molecules. Rotaxanes and pseudorotaxanes that incorporate metal ions represent a particularly interesting class of supramolecular species that might display a rich variety of physicochemical properties such as redox, optical, and magnetic behavior. Metal ion directed threading may also be used for constructing linear arrays of metal ions with precisely defined interionic distances, for example, inorganic rack-type architectures.[9] This approach may additionally provide access to self-assembled pseudorotaxane racks that incorporate linear strings of metal ions in oxidation states not normally accessible in the presence of nonmacrocyclic ligand analogues due to dissociative instability.

We here report the high-yield formation (Scheme 1) and X-ray crystallographic investigation of the trinuclear [4]pseudorotaxane rack **1**. In previous work on metallorotaxanes incorporating linear oligobipyridines as the central unit,[10] the metal ions were alternately situated on opposite sides of the ligand rack in a *trans* conformation in the solid state. In contrast, **2**, which incorporates pyridazine metal ion bridging units, is expected to yield a pseudorotaxane rack in which the metal ions are situated on the same side, that is, an all *syn* relationship with shorter internuclear separations. This structural modification may increase electronic communication between the metal centers and render these systems more attractive candidates for molecular-device components.



Scheme 1. Self-assembly of the tricopper pseudorotaxane [3]rack **1**.

Mixture of **2**, **3**, and $[Cu(MeCN)_4]PF_6$ in a 1:3:3 stoichiometric ratio in CH_2Cl_2/MeCN (1/1) resulted in the formation of **1** in greater than 80% yield. The rigid-rod ligand **2** and the macrocyclic ligand **3** were prepared as previously reported.[11, 12] The identity of the reaction product was established with ^1H and ^{13}C NMR spectroscopy, FAB-MS (Table 1), and X-ray crystallography. The ^1H NMR spectrum was particularly informative and showed **3** to be in two different chemical environments. For example, the *ortho* and *meta* phenyl-ring

Table 1. Physical and spectroscopic data for $\mathbf{1}(PF_6)_3$.

^1H NMR (CD_3NO_2, 500 MHz, 20 °C): $\delta = 9.212$ (d, J(H3′,H4′) = 9.3 Hz, **2**-H3′), 9.159 (d, J(H4′,H3′) = 9.3 Hz, **2**-H4′), 8.527 (d, J(H3,H4) = 8.1 Hz, **2**-H3), 8.192 (d, J(H4,H3) = J(H7,H8) = 8.3 Hz, $\mathbf{3}_{outer}$-H4/7), 8.153 (t, J(H3,H4,H5) = 7.9 Hz, **2**-H4), 8.096 (d, J(H4,H3) = J(H7,H8) = 8.4 Hz, $\mathbf{3}_{inner}$-H4/7), 7.908 (s, $\mathbf{3}_{inner}$-H5/6), 7.812 (s, $\mathbf{3}_{outer}$-H5/6), 7.498 (d, J(H3,H4) = J(H8,H7) = 8.3 Hz, $\mathbf{3}_{outer}$, H3/8), 7.444 (d, J(H5,H4) = 7.7 Hz, **2**-H5), 7.284 (d, J(H3,H4) = J(H8,H7) = 8.3 Hz, $\mathbf{3}_{inner}$-H3/8), 6.678 (d, J(*ortho*-H,*meta*-H) = 8.6 Hz, $\mathbf{3}_{outer}$-*ortho*-H), 6.422 (d, J(*ortho*-H,*meta*-H) = 8.7 Hz, $\mathbf{3}_{inner}$-*ortho*-H), 6.215 (d, J(*meta*-H,*ortho*-H) = 8.8 Hz, $\mathbf{3}_{inner}$-*meta*-H), 6.171 (d, J(*meta*-H,*ortho*-H) = 8.7 Hz, $\mathbf{3}_{outer}$-*meta*-H), 4.125–3.600 (m, $\mathbf{3}_{inner/outer}$-H(CH_2)), 1.711 (s, **2**-CH_3). All CH_3 and ring proton signals for **2** in the ^1H NMR spectrum of **1** represent magnetically and chemically equivalent pairs of protons on the ligand; ^{13}C NMR (CD_3NO_2, 75 MHz, 20 °C): $\delta = 165.839$, 165.346, 163.068, 162.577, 162.289, 161.219, 157.959, 152.301, 147.940, 147.499, 144.381, 143.766, 143.249, 136.826, 135.345, 134.143, 133.980, 133.936, 133.752, 133.597, 133.074, 132.944, 132.241, 131.643, 129.630, 129.293, 127.772, 119.691, 119.220 (aromatic C atoms); 75.690, 75.608, 75.457, 75.346, 75.268, 74.617, 74.141, 73.496 (CH_2); 28.496 (CH_3); FAB-MS (CH_2Cl_2): m/z (relative intensity in %) = 2520.6 (0.5) $[Cu_3(\mathbf{2})(\mathbf{3})_3](PF_6)_2^+$, 2375.6 (0.7) $[Cu_3(\mathbf{2})(\mathbf{3})_3](PF_6)^{\cdot+}$, 2230.6 (0.1) $[Cu_3(\mathbf{2})(\mathbf{3})_3]^{\cdot\cdot+}$, 1745.4 (2.3) $[Cu_2(\mathbf{2})(\mathbf{3})_2](PF_6)^+$, 1600.5 (1.1) $[Cu_2(\mathbf{2})(\mathbf{3})_2]^{2+}$, 1115.3 (1.2) $[Cu_3(\mathbf{2})(\mathbf{3})_3]^{\cdot 2+}$, 969.3 (12.0) $[Cu(\mathbf{2})(\mathbf{3})]^+$, 629.2 (100) $[Cu(\mathbf{3})]^+$; UV/Vis (CH_2Cl_2): λ (ε in $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$) = 286.0 (81320), 321.0 (102480), 478.0 nm (8073); elemental analysis calcd for $C_{122}H_{118}Cu_3F_{18}N_{12}O_{18}P_3$: C 54.97, H 4.46, N 6.30; found: C 54.79, H 4.33, N 6.24.

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