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Dimerization of β-Diketiminato Calcium Complexes through Dihapto-Acetylide Ligation

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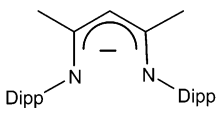
The "selective" protonolysis of the β-diketiminato calcium derivative [Ca{(NDippCMe)$_2$CH}{N(SiMe$_3$)$_2$}(THF)] (Dipp = $C_6H_3{}^iPr_2$-2,6) with a selection of terminal alkynes has produced a series of dimeric acetylides [Ca{(NDippCMe)$_2$CH}{μ-C≡CR}]$_2$, which have been characterized in solution and in the solid state. The asymmetry of the Ca−C−Ca′ bridges is subtly dependent upon the extent of "side-on" (π-type) interaction between the acetylide unit and the Ca′ centers.

Introduction

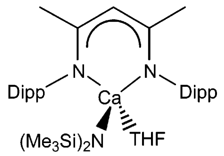
Although a structural understanding of the heavier alkaline earth elements (Ae = Ca, Sr, Ba) has advanced significantly in recent years, a useful and widely applicable reaction chemistry has yet to emerge.[1] This lacuna of information may be attributed to the large size and electropositive nature of the metals. Group 2 organometallic and coordination complexes are highly labile species, which undergo increasingly facile Schlenk-like redistribution processes in solution with increasing metal radius and electropositive character. Unless polydentate and/or bulky and kinetically stabilizing ligands are employed, there exists a tendency toward the formation of ill-defined oligomeric or polymeric species.[2]

Structurally characterized heavier alkaline earth organometallic compounds that contain carbon−Ae σ-bonded substituents can be crudely divided into four categories: (i) homoleptic compounds that contain bulky σ-bonded substituents in order to stabilize the labile metal center;[3] (ii) homoleptic compounds containing less sterically demanding C-centered ligands, but stabilized by a neutral polydentate ligand;[4] (iii) "ate" complexes in which the ligand is part of a three-center/two-electron link to a heterometallic center;[5] (iv) heteroleptic compounds that rely on the use of a sterically demanding and/or polydentate monoanionic ligand set to impart stability to the complex.[6]

The latter class of heteroleptic species offers the best opportunity for the development of a controlled reaction chemistry. The application of a supporting ligand that is kinetically stable toward solution redistribution provides a platform to study the reaction chemistry of simple σ-bonded substituents and, ultimately, a means to influence the stereochemical outcome of the reaction.[7] Recent studies within our laboratories and elsewhere have sought to employ transamination methodology to synthesize well-defined heteroleptic species of the form LAeX, where X is a simple and sterically undemanding σ-bonded substituent and L is a polydentate *monoanionic* ligand capable of providing kinetic stability to the resultant complex.[8]



I



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Dipp = $C_6H_3{}^iPr$-2,6

The use of β-diketiminato ligands such as **I** has been widely adopted in recent years.[9] An appraisal of the β-diketiminato-stabilized calcium amide **1**, originally reported by Chisholm et al. in the context of lactide

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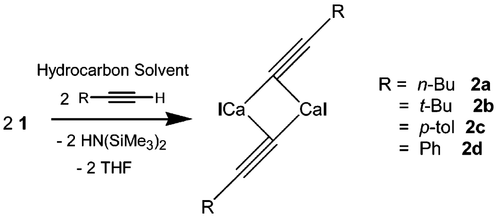
Scheme 1



polymerization catalysis, suggested that **I** may provide sufficient (kinetic) solution stability to block deleterious Schlenk-like redistribution processes between the calcium metal centers. We have shown furthermore that complex **1** is a convenient synthon to develop new heteroleptic calcium species via selective protonolysis of the amide group by substrates with a lower pK_a than that of bis(trimethylsilyl)amine.[8c] Terminal alkynes satisfy this criterion, and examination of the literature revealed that the only calcium acetylides to have been structurally characterized, $[\{[(^iPr)_4C_5H]Ca(\mu\text{-}C{\equiv}CPh)(thf)\}_2]$ and $[Ca([18]crown\text{-}6)(C{\equiv}CSiPh_3)_2]$, were both synthesized by a similar transamination methodology.[4a,6] Although the study of transition metal acetylides has blossomed since the 1980s,[10] the limited precedent provided by these two compounds highlights the relative dearth of structural information regarding calcium acetylides. Our motivation for this work is also rooted in our more general exploration of potentially "lanthanide analogous" reaction chemistry of the heavier alkaline earth elements.[11] In the present context for example, predominantly ionic 4f-element acetylides, $[Cp^*{}_2LnC{\equiv}CR]$ (Ln = Ce, La), are capable of multiple insertion chemistry and/or catalytic "head-to-tail" oligomerization and polymerization of terminal alkynes.[12] As an initial step toward a more general exploration of their reaction chemistry, we present here a series of unsolvated and dimeric calcium acetylides, $[\mathbf{I}CaC{\equiv}CR]_2$ (R = *n*-Bu, *t*-Bu, *p*-tol, Ph). These compounds may be synthesized straightforwardly by addition of the terminal alkyne to the heteroleptic precursor **1** in hydrocarbon solvents at room temperature (Scheme 1).

Results and Discussion

An initial NMR scale experiment in C_6D_6 confirmed that the stoichiometric reaction between **1** and hex-1-yne led to quantitative formation of the desired heteroleptic calcium acetylide with liberation of bis(trimethylsilyl)amine and tetrahydrofuran. In contrast to our previous experience with *β*-diketiminato-ligated calcium amides,[8d] this solution exhibited no apparent tendency toward solution redistribution to the known homoleptic calcium species $[Ca\{(NDippCMe)_2CH\}_2]$[8b,13] (Dipp = $C_6H_3{}^iPr_2$-2,6) and encouraged us to extend this chemistry to a preparative scale for a range of terminal alkynes.

Table 1. Comparative IR Data for 2a−d

	ν(C≡C) (cm^{-1})		
	ICa≡R	R≡H	$\Delta\nu$ (cm^{-1})
2a	2048	2118	70
2b	2029	2106	77
2c	2034	2110	76
2d	2040	2111	71

Room-temperature addition of a hexane solution of the appropriate acetylene to a hexane solution of **1** followed by concentration and crystallization resulted in the isolation of compounds **2a**−**d** as colorless crystalline solids. Although stable under an inert atmosphere, the compounds are extremely sensitive to moisture and liberate the free acetylene within seconds of exposure to the atmosphere. The compounds are soluble in hydrocarbon solvents with solubility decreasing across the series in the order **2a** > **2b** > **2c** > **2d**. The phenyl acetylide derivative **2d** demonstrated only very limited solubility in toluene, precluding the acquisition of satisfactory NMR data. Due to the novel nature of the dimeric compounds (vide infra), the use of polar aprotic solvents was avoided to prevent adduct formation and dimer cleavage.

Infrared analysis of compounds **2a**−**d** confirmed the presence of the ethynyl moiety. The ν(C≡C) frequencies are similar to those reported for the known dimeric and polymeric calcium acetylides $[\{[(^iPr)_4C_5H]Ca(\mu\text{-}C{\equiv}CR')(thf)\}_2]$ and $[\{Ca(C{\equiv}CPh)_2\}_n]$ (Table 1).[6,14] Comparison of these frequencies with those of the free terminal alkynes shows that, upon deprotonation and complexation, the alkyne stretch is shifted to lower frequency, synonymous with a lengthening of the C≡C bond.

The aliphatic acetylide derivatives **2a** and **2b** were sufficiently soluble to warrant variable temperature NMR analysis in deuterated toluene. In both cases a small NOE was observed between the protons of the alkynyl moiety and the isopropyl methine protons of the ligand, implying that in solution the aromatic groups of the ligand flank the acetylide *n*-butyl and *tert*-butyl residues.

At 238 K the *i*-Pr environments of the *β*-diketiminato ligand in the ^1H NMR spectrum of compound **2b** split, giving rise to distinct resonances for each isopropyl-methine and diastereotopic isopropyl-methyl environment. Although similar low-temperature studies undertaken on samples of **2a** revealed no such decoalescence of proton environments at the low-temperature limit of 192 K, a pronounced broadening was observed and it is probable that decoalescence would occur at lower temperatures. These observations may be rationalized to be a result of hindered rotation about the N−Ar bond and the observation of meta-stable rotamers compared to the NMR time scale. The higher activation energy for the rotation about the N−Ar bond of the *tert*-butyl derivative **2b** over the *n*-butyl derivative **2a** can be ascribed to the greater steric demands of the former.

Crystals of compounds **2a**−**d** suitable for X-ray diffraction analysis were grown by slow cooling of concentrated hexane or toluene solutions. Although disorder inherent in the butyl chains of the hexynyl moieties of

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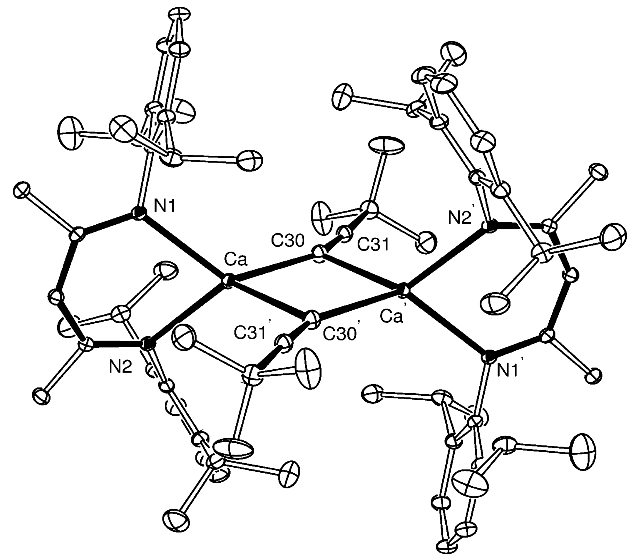

Figure 1. Thermal ellipsoid plot of **2b** (20% probability). H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ca−N2 2.327(1), Ca−N1 2.339(1), Ca−C30 2.496(2), Ca−C30′ 2.510(1), Ca−C31′ 3.167(1), C30−C31 1.216(2), N2−Ca−N1 82.89(4), N2−Ca−C30 117.10(4), N1−Ca−C30 123.66(4), N1−Ca−C30′ 124.30(4), C30−Ca−C30′ 89.73(5), N2−Ca−C30′ 123.06(4), N2−Ca−C31′ 109.71(4), N1−Ca−C31′, 109.81(4), C30−Ca−C31′ 110.63(4), C30−C31−C32 176.23(15), C31−C30−Ca 157.99(12), C31−C30−Ca′ 111.61(11).

compound **2a** precluded satisfactory refinement, the structure was unambiguously dimeric and similar to those elucidated for **2b**−**d** (vide infra). Satisfactory single-crystal X-ray data were collected for compounds **2b**−**d**. The results of the analyses of **2b** and **2c** are illustrated in Figures 1 and 2 (the structure of **2d** is very similar to that of **2c**), and selected bond length and angle data for all three compounds are provided in the figure captions. Compounds **2b**−**d** crystallize in the dimeric form established for **2a** and exhibit a slightly asymmetric but planar four-membered core with sp-hybridized acetylides that bridge the calcium centers via three-center, two-electron bonds. The ethynyl moieties display an apparent π-interaction with each calcium center, resulting in a series of asymmetrically bridged D_2-symmetric dimers. Further coordination is exclusively provided by the N,N chelate of the β-diketiminato ligand.

The $Ca-C_\alpha$, $Ca-C_\alpha'$, and $C_\alpha{\equiv}C_\beta$ distances are displayed in Table 2 and are in close correspondence with the previously reported and structurally characterized calcium acetylides.[4,6] The apparent π-interaction causes only minor perturbation to the symmetry of the Ca−C−Ca′ bridge, and both the respective $Ca-C_\alpha$ and $Ca-C_\alpha'$ distances are indicative of a strong interaction with both calcium centers. The bond lengths and angles around the β-diketiminato chelate, the Ca−N distances, and the N(1)−Ca−N(2) bite angles are similar to those of the heteroleptic precursor **1** and primary amido and anilido calcium derivatives supported by **I**.[8]

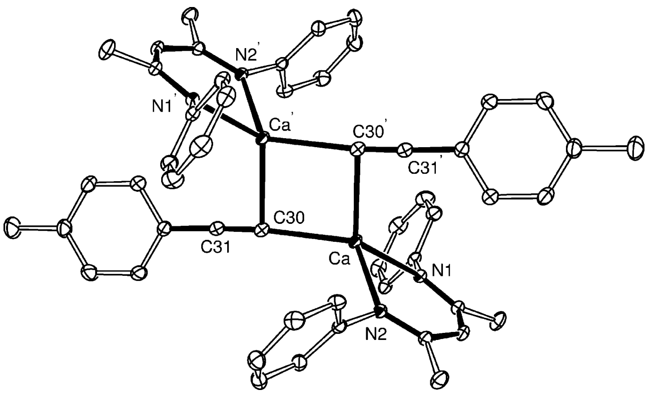

Figure 2. Thermal ellipsoid plot of **2c** (20% probability). H atoms and ^{i}Pr methyl groups omitted for clarity. Selected bond lengths (Å) and angles (deg). **2c**: Ca−N2 2.313(1), Ca−N1 2.319(1), Ca−C30 2.492(2), Ca−C30′ 2.530(2), Ca−C31′ 2.895(2), C30−C31 1.221(2), N2−Ca−N1 80.24(5), N2−Ca−C30 118.16(6), N1−Ca−C30 130.00(6), N1−Ca−C30′ 123.54(5), C30−Ca−C30′ 88.91(6), N2−Ca−C30′ 119.88(6), N2−Ca−C31′ 104.82(5), N1−Ca−C31′ 103.70(5), C30−Ca−C31′ 113.77(6), C30−C31−C32 178.06(19), C31−C30−Ca 174.37(15), C31−C30−Ca′ 94.53(13). **2d**: Ca−N2 2.318(1), Ca−N1 2.311(1), Ca−C30 2.505(2), Ca−C30′ 2.535(2), Ca−C31′ 2.940(2), C30−C31 1.224(2), N2−Ca−N1 80.63(4), N2−Ca−C30 130.34(5), N1−Ca−C30 117.93(5), N1−Ca−C30′ 117.08(5), C30−Ca−C30′ 89.70(5), N2−Ca−C30′ 124.20(5), N2−Ca−C31′ 103.86(4), N1−Ca−C31′ 103.34(4), C30−Ca−C31′ 114.11(5), C30−C31−C32 178.04(18), C31−C30−Ca 172.85(13), C31−C30−Ca′ 96.68(11).

Table 2. Metrical Data for 2b−d, Relating to the Asymmetry of the Ca−C−Ca′−C′ Dimer

	bond lengths (Å)			bond angles (deg)		
	$Ca-C_\alpha$ $Ca'-C_\alpha$	$C_\alpha{\equiv}C_\beta$	$Ca'-C_\beta$	$C_\beta-C_\alpha-Ca$ (θ)	$C_\beta-C_\alpha-Ca'$ (φ)	($\theta - \varphi$)
2b	2.496(2) 2.510(1)	1.216(2)	3.167(1)	157.99(12)	111.61(11)	46.4
2c	2.492(2) 2.530(2)	1.221(2)	2.895(2)	174.4(2)	94.53(13)	79.9
2d	2.505(2) 2.535(2)	1.224(2)	2.940(2)	172.85(13)	96.68(11)	76.2

Dimeric acetylide derivatives of the lighter members of group 2 and group 13 have been known for some time. The trimethylamine adduct of methylpropynylberyllium crystallizes such that the acetylide group is nearly perpendicular to the Be−Be vector.[15] In contrast, diphenyl(phenylethynyl) aluminum forms a dimer in which the two metals and the two acetylide α-carbons produce a rectangular array, a feature that was interpreted as bonding via one Al−C σ-bond and overlap between one carbon 2p-π orbital with an aluminum $3p_z$ orbital.[16] Although such covalent descriptions are not applicable to the highly ionic compounds **2a**−**d**, these two extremes may be considered to reflect the role of the acetylide ligand as a one- or three-electron donor, respectively. Application of a similar rationale to the asymmetry observed in the structures of **2b**−**d** is therefore strongly suggestive of a π-bonding component, and indeed similar observations have been made regarding the structures of dimeric 4f-element acetylides.[17] Table 2 illustrates this asymmetry in terms of the respective $Ca-C_\alpha-C_\beta$

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(θ) and Ca′−C$_\alpha$−C$_\beta$ (φ) angles of **2b**−**d**. For completely symmetric bridging (containing no π-bonding component) the C$_\alpha$−C$_\beta$ bond should lie perpendicular to the metal−metal vector ($\theta = \varphi$), while a side-on π-interaction would be evidenced by values of φ and θ of 90° and 180°, respectively. The ($\theta - \varphi$) data illustrated in Table 2 and the similarity of the Ca′−C$_\beta$ (Ca′−C(31)) bond distances (**2b**, 3.167(1); **2c**, 2.940(2); **2d**, 2.895(2) Å) to the Ca−C$_{\text{acetylene}}$ interactions observed in the alkyne-adducted calcocene, [Cp*$_2$Ca(Me$_3$SiC≡C−C≡CSiMe$_3$)], (Ca−C ca. 3 Å) are also particularly supportive of a significant π-component in the bridged structures of **2c** and 2**d**.[18]

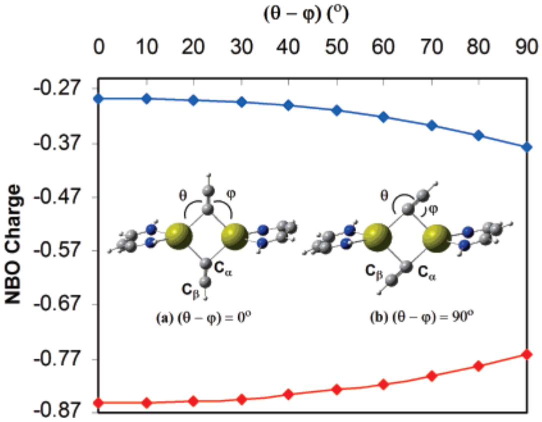

Figure 3. Calculated variation of (NBO) negative charge on C$_\alpha$ (red) and C$_\beta$ (blue) for 0° < ($\theta - \varphi$) < 90°.

The nature of the (side-on) acetylide−calcium interactions present in the structures of **2a**−**d** was investigated through DFT calculations performed on the model complex [Ca{(NHCH)$_2$CH}{C≡CH}]$_2$, **3**, using the B3LYP density functional theory and LANL2DZ pseudopotentials (and basis set) implemented in Gaussian 03.[19] It is well recognized that the formulation of a definitive description of the bonding within heavier alkaline earth complexes is extremely challenging.[20] A series of single-point energy calculations (based upon atomic coordinates provided by the crystallographic analysis of **2d**), in which the ($\theta - \varphi$) value for the bridging acetylide unit was varied in 5° increments between 0° and 90°, illustrated that there was little change in the overall energy of the system for ($\theta - \varphi$) values 0° < ($\theta - \varphi$) < 50° (ca. 1 kJ mol^{-1}). Extension to ($\theta - \varphi$) values beyond 50° produced a modest but *destabilizing* influence within the dimeric structure, amounting to an overall increase of some 6−10 kJ mol^{-1} for ($\theta - \varphi$) values commensurate with those observed in the structures of **2c** and **2d** (ca. 170−175°). These values are similar to those computed for the energy difference between the bent and linear structures of mononuclear calcocenes.[21] The modest energy barriers implied from this analysis of the simple model compound **3** completely neglect the steric influence of both the N-aryl substituents of the β-diketiminato chelate and the alkyl/aryl residues of the Ca-bound acetylide unit. The crystallographic results emphasize therefore (apparent from the more acute ($\theta - \varphi$) value observed for **2b**) that steric factors are likely to be highly influential in the precise structures adopted by **2a**−**d**. Examination of the charge distribution within **3** by a natural bond orbital (NBO) analysis provided a qualitative rationale for the "side-on" acetylide binding within **2a**,**b**. The charge on the Ca center (ca. +1.83) is unaffected for all values of ($\theta - \varphi$) and is suggestive of essentially ionic bonding.[22] The data presented in Figure 3 illustrate the variation in negative charge on the C$_\alpha$ (red curve) and C$_\beta$ (blue curve) carbons of the ethynyl group for values of ($\theta - \varphi$) between the extremes of 0° and 90°. It can be observed that higher values of ($\theta - \varphi$) enhance a relatively minor dissipation of negative charge over both acetylide carbon centers. The bent geometry of [(C$_5$Me$_5$)$_2$Ae] metallocenes has been ascribed to polarization and dipole formation in the large Ae^{2+} cations induced by the negatively charged cyclopentadienyl rings.[21] On this basis the structures determined for **2a**−**d** can be postulated as a similar compromise between a maximization of the ionic/electrostatic interaction between the large polarizable Ca^{2+} center and the acetylide unit and the steric bulk of the alkynyl C$_\beta$ substituent. This view of the structures of **2a**−**d** is consistent therefore with previous ionic models proposed to account for the structural features within systems containing heavier alkaline earth cations engaged in polyhapto interactions with unsaturated ligand systems.[1] We are continuing to study the reactivity of these well-defined and easily prepared calcium organometallics and will report the results of these investigations in future publications.

Experimental Section

All manipulations involving alkaline earth metals were carried out using standard Schlenk and glovebox techniques under an inert atmosphere of either dinitrogen or argon. All solvents were distilled under dinitrogen and dried with conventional drying agents. Terminal alkynes were purchased from Sigma-Aldrich and freeze−thaw−degassed before use. NMR spectra were recorded at 270 or 500 (^{1}H) and 125.8 (^{13}C) MHz from samples in d_8-toluene; chemical shifts are given relative to SiMe$_4$. Repeated attempts to accumulate mass spectral data on isolated compounds were unsuccessful due to their air- and moisture-sensitivity. Attempts to acquire elemental analysis data for compounds **2a**−**d** were only partially successful due to the extremely moisture-sensitive nature of the compounds. The ligand precursor **I**H and

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heteroleptic calcium amide **1** were synthesized by literature procedures.[8a,b,23]

Synthesis of [ICa(C≡C−R)]$_2$, 2a−d. To a stirred solution of calcium amide **1** (0.5 g, 0.72 mmol) in a hydrocarbon solvent under nitrogen was added a stoichiometric quantity of the acetylene as a solution in the same solvent. In all cases the product crystallizes directly from hexane solutions. X-ray quality crystals of **2a** and **2b**−**d** were acquired by recrystallization from hexane and toluene, respectively.

2a: Yield: 0.14 g, 0.24 mmol, 34%. Mp: 93−94 °C (dec). ^{1}H NMR (ppm): δ 0.78−0.84 (m, 3H, CH_3CH$_2$), 1.02 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(Me)$_2$), 1.15 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(Me)$_2$) 1.09−1.24 (m, 4H, CH_2CH_2) 1.52 (s, 6H, C(Me)), 1.82 (t, 2H, $^3J_{HH}$ = 7.1 Hz, CH_2C≡C), 3.11 (m, 4H, $^3J_{HH}$ = 6.8 Hz, CH(Me)$_2$), 4.63 (s, 1H, C(Me)CH), 6.99−7.10 (m, 6H, ArH). ^{13}C NMR (ppm): δ 14.4, 21.1, 23.0, 24.9, 25.9, 28.7, 32.1, 94.7, 121.5, 124.4, 125.5, 127.0,142.6,145.2, 166.4. IR cm^{-1} (KBr disk): 3058, 2961, 2923, 2868, 2048, 1622, 1551, 1461, 1318, 1255, 1171, 1100, 1020, 788, 758.

2b: Yield: 0.15 g, 0.28 mmol, 39%. Mp: 141 °C (dec). ^{1}H NMR (ppm): δ 1.00 (s, 9H, C(CH_3)$_3$), 1.08 (d, 12H, $^3J_{HH}$ = 7 Hz, CH(Me)$_2$), 1.13 (d, 12H, CH(Me)$_2$), 1.51 (s, 6H, C(Me)), 3.16 (m, 4H, CH(Me)$_2$), 4.65 (s,1H, C(Me)CH), 6.90−7.10 (m, 6H, ArH). ^{13}C NMR (ppm): δ 14.7, 24.9, 25.9, 28.7, 32.4, 94.7, 123.9, 124.4, 125.3, 126.2, 142.5, 146.2, 166.5. IR cm^{-1} (KBr disk): 3061, 2963, 2928, 2869, 2029, 1623, 1551, 1514, 1461, 1436, 1405, 1316, 1255, 1171, 1100, 788, 759.

2c: Yield: 0.12 g, 0.27 mmol, 38%. Mp: 48−50 °C (dec). ^{1}H NMR (ppm): δ 1.14 (d, 12H, CH(Me)$_2$), 1.24 (d, 12H, CH(Me)$_2$), 1.71 (s, 6H, C(Me)), 2.15 (s, 3H, p-Me), 3.00 (m, 4H, CH(Me)$_2$), 4.81, (s, 1H, C(Me)CH), 7.00−7.22 (m, 10H, ArH). ^{13}C NMR (ppm): 19.9, 23.4, 28.5, 28.6, 94.4, 114.9, 123.9, 125.1, 125.4, 127.7, 127.9, 137.5, 142.5, 144.1, 165.5. IR cm^{-1} (KBr disk): 3057, 2962, 2926, 2867, 2040, 1654, 1624, 1551, 1517, 1461, 1459, 1438, 1405, 1364, 1317,1260, 1170, 1100, 1020, 935, 816, 788, 757.

2d: Yield: 0.12 g, 0.21 mmol, 29%. Mp: 84−85 °C (dec). IR cm^{-1} (KBr disk): 3058, 2962, 2867, 2034, 1622, 1551, 1462, 1437, 1403, 1318, 1256, 1172, 1100, 925, 788, 757, 691. Anal. Calcd for $C_{74}H_{92}Ca_2N_4$: C 79.52, H 8.30, N 5.01. Found: C 79.92, H 8.32, N 5.02.

Crystal Structure Determinations. Data for **2b**−**d** were collected at 173 K on a Nonius KappaCCD diffractomer, λ(Mo Kα) = 0.71073 Å. An absorption correction (MULTISCAN) was applied. The structures were solved by direct methods (SHELXS-97)[24] and refined by full matrix least squares (SHELXL-97)[25] with non-H atoms anisotropic and H atoms included in riding mode.

Crystal Data. 2b: $C_{70}H_{100}Ca_2N_4 \cdot 2(C_7H_8)$, M = 1261.97, triclinic, space group $P\bar{1}$ (No. 2), a = 11.9217(2) Å, b = 13.2905(2) Å, c = 13.4317(2) Å, α = 89.254(1)°, β = 72.703(1)°, γ = 71.976(1)°, U = 1924.91(5) Å^3, Z = 1, D_c = 1.09 g cm^3, 30 434 reflections, 8687 unique (R_{int} 0.039), 7795 with $I > 2\sigma(I)$. R1, wR2 0.045, 0.113 [$I > 2\sigma(I)$] and 0.051, 0.117 (all data). **2c**: $C_{76}H_{96}Ca_2N_4$, M = 1145.73, monoclinic, space group $P2_1/n$ (No. 14), a = 14.9183(3) Å, b = 13.1452(2) Å, c = 18.3729(2) Å, β = 103.916(1)°, U = 3497.25(12) Å^3, Z = 2, D_c = 1.09 g cm^3, 43 924 reflections, 6160 unique (R_{int} 0.045), 5147 with $I > 2\sigma(I)$. R1, wR2 0.041, 0.101 [$I > 2\sigma(I)$] and 0.053, 0.109 (all data). **2d**: $C_{74}H_{92}Ca_2N_4$, M = 1117.68, monoclinic, space group $P2_1/n$ (No. 14), a = 15.0572(3) Å, b = 13.0076(3) Å, c = 17.5209(4) Å, β = 100.482(1)°, U = 3374.34(13) Å^3, Z = 2, D_c = 1.10 g cm^3, 23 366 reflections, 5859 unique (R_{int} 0.033), 5121 with $I > 2\sigma(I)$. R1, wR2 0.040, 0.098 [$I > 2\sigma(I)$] and 0.048, 0.103 (all data).

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Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge at http://pubs.acs.org.

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