= 421 nm, ϵ = 288 000).[18] This peak is flanked by exceptionally strong N- and Q-like bands at higher and lower energies. As would be expected for a larger π system, both the lowest energy Q-like absorption (λ_{max} = 767.5 nm, ϵ = 41 200) and emission (λ_{max} 792 nm) bands of **3·Cl** are substantially red-shifted (by ca. 200 nm!) as compared to those of typical cadmium porphyrins.[18,19]

When the above metal insertion was repeated with cadmium nitrate, a complex was obtained in roughly 30% yield, which on the basis of microanalytical data,[15] was formulated as the protonated complex **3·NO₃·(HNO₃)**. Upon treatment with excess pyridine and recrystallization from chloroform–hexane, the bis-pyridine adduct **4·NO₃**, with spectral properties essentially identical with **3·Cl**, was isolated as dark green crystals.[15] The molecular structure of **4·NO₃**, determined by X-ray diffraction analysis, confirms the aromatic nature of the ligand (Figure 1).[20] The central five nitrogen donor atoms of **4** are essentially coplanar and define a near circular cavity with a center-to-nitrogen radius of ca. 2.39 Å (cf. Figure 2), which is roughly 20% larger than that found in metalloporphyrins.[21] The Cd atom lies in the plane of the central N_5 binding core. The structure of the "expanded porphyrin" **4** thus differs dramatically from that of CdTPP[16,22] or CdTPP·(dioxane)₂,[23] in which the cadmium atom lies out of the porphyrin N_4 donor plane (by 0.58 and 0.32 Å, respectively). Moreover, in contrast to cadmium porphyrins, for which a five-coordinate square-pyramidal geometry is preferred and to which only a single pyridine molecule will bind,[24] in **4·NO₃** the cadmium atom is *seven-coordinate*, being complexed by *two apical pyridine ligands*. The configuration about the Cd atom is thus *pentagonal bipyrimidal*; a rare but not unknown geometry for cadmium(II) complexes.[25]

Under neutral conditions complexes **3** and **4** appear to be more stable than cadmium porphyrins: Whereas treatment of CdTPP or CdTPP(pyr) with aqueous Na_2S leads to cation loss and precipitation of CdS, in the case of **3** and **4** no demetallation takes place. (Exposure to aqueous acid, however, leads to hydrolysis of the macrocycle.) Indeed, we have been unable to prepare the free-base ligand **2** by demetallation. The tripyrroledimethine-derived free-base ligand **2** was therefore synthesized directly from **1** by stirring in air-saturated chloroform-methanol containing *N,N,N'*-tetramethyl-1,8-diaminonaphthalene.[15] Although the yield is low ($\leq$12%),[26] once formed, **2** appears to be quite stable: It undergoes decomposition far more slowly than **1**.[13] Presumably, this is a reflection of the aromatic stabilization present in **2**. A

further indication of the aromatic nature of the free-base "expanded porphyrin" **2** is the observation of an internal pyrrole NH signal at δ = 0.90, which is shifted upfield by over 10 ppm as compared to the pyrrolic protons present in the reduced macrocycle **1**.[13] This shift parallels that seen when the sp³-linked macrocycle, octaethylporphyrinogen (δ(NH) = 6.9),[27] is oxidized to the corresponding porphyrin, H_2OEP (δ(NH) = −3.74).[17] This suggests that the diamagnetic ring current present in **2** is similar in strength to that of the porphyrins.

The aromatic "expanded porphyrin" system reported here could provide an interesting complement to the existing rich coordination chemistry of porphyrins. For instance, by using methods similar to those described here, we have prepared and characterized zinc(II), manganese(II), mercury(II), and neodymium(III) complexes of **2**[15] and are now exploring the chemical properties of these systems.

Supplementary Material Available: Characterization data for new compounds, ¹H NMR and UV–vis spectra for **2** and **3·Cl**, atom labeling scheme for **4**, X-ray experimental data for **4·NO₃**, and tables of atomic thermal factors, atomic positional parameters, and bond distances and angles (18 pages). Ordering information is given on any current masthead page.

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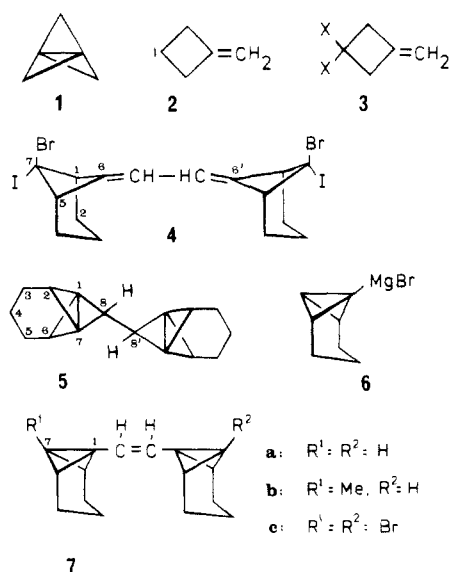
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(26) Other oxidants, including DDQ, Ag₂O, I₂, PtO₂, PbO₂, SeO₂, and Ph₃CBF₄, either failed to react or gave rise only to decomposition products.

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8,8'-Bis(tetracyclo[5.1.0.0^{1,6}.0^{2,7}]octane), a Coupled [1.1.1]Propellane: Synthesis and Structure

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Our recent observation that the [1.1.1]propellane framework **1** is accessible by carbene or carbenoid cyclization of type **2**[1] has meanwhile proved to be an efficient synthetic route to derivatives of **1**. However, dihalides of type **3**, the precursors of **2**, are not easily available. Accordingly, we have searched for a new method of synthesizing type **3** compounds. We report here on the facile access to **4** and on its reductive cyclization to the coupled [1.1.1]propellane **5**.

4 was obtained in three steps starting from the Grignard reagent **6**, which was converted into *cis*-**7a** in 42% yield by cross-coupling with *trans*-1,2-dichloroethylene under Ni(0) catalysis:[2–4] [¹H NMR (CDCl₃) δ 1.38 (m, 14 H), 2.70 (m, 4 H), 5.38 (s, 2 H); ¹³C NMR (CDCl₃) δ 18.20 (d, C-7), 20.08 (s, C-1), 20.63 (t, C-3, C-5), 21.20 (t, C-4), 45.74 (d, C-2, C-6), 127.46 (d, −CH=); HRMS calcd for $C_{16}H_{20}$ 212.1565, found 212.159]. The cis configuration of **7a** was established by ¹H NMR spectroscopy after introduction of a methyl group at C-7 giving **7b** which showed

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(3) 1.0 mol % of dichloro[1,2-bis(diphenylphosphino)ethane]nickel(II) was used.

(4) Experimental procedures are included as Supplementary Material.

Communications to the Editor

J. Am. Chem. Soc., Vol. 110, No. 16, 1988 5589
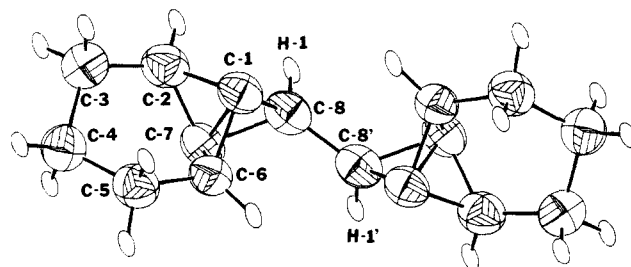

Figure 1, ORTEP plot of 5. The thermal ellipsoids are drawn at the 50% probability level except for the hydrogens which are drawn arbitrarily small for clarity. Selected interatomic distances and angles are as follows: Distances (Å): C_1–C2 1.517 (2); C1–C6 1.513 (2); C1–C7 1.577 (1); C1–C8 1.515 (2); C2–C3 1.505 (1); C2–C7 1.524 (1); C3–C4 1.522 (1); C4–C5 1.512 (1); C5–C6 1.508 (2); C6–C7 1.529 (1); C7–C8 1.515 (1); C8–C8′ 1.494 (2). Angles (deg): C2–C1–C6 95.51 (7); C2–C1–C7 58.97 (5); C2–C1–C8 95.66 (6); C6–C1–C7 59.24 (4); C6–C1–C8 96.20 (6); C7–C1–C8 58.66 (4); C1–C2–C3 120.25 (8); C1–C2–C7 62.49 (6); C3–C2–C7 119.58 (8); C2–C3–C4 111.21 (8); C3–C4–C5 110.79 (8); C4–C5–C6 111.46 (6); C1–C6–C5 118.58 (7); C1–C6–C7 62.46 (5); C5–C6–C7 119.72 (7); C1–C7–C2 58.54 (5); C1–C7–C6 58.30 (4); C1–C7–C8 58.62 (4); C2–C7–C6 94.63 (6); C2–C7–C8 95.37 (6); C6–C7–C8 95.56 (6); C1–C8–C7 62.72 (5); C1–C8–C8′ 123.76 (4); C7–C8–C8′ 121.53 (9); dihedral angles: C2–C1–C7–C6 119.26; C2–C7–C1–C8 120.09; C6–C1–C7–C8 120.65; H1–C8–C8′–H1′ 93.23 (5).

an olefinic coupling constant of 10.0 Hz.[5] The hydrocarbon **7a** was brominated at the bridgehead positions after metalation with 2.0 equiv of butyllithium in ether followed by reaction with 2.0 equiv of tosyl bromide, affording **7c** in 43% isolated yield[4] [¹H NMR (CDCl₃) δ 1.45 (m, 12 H), 2.88 (m, 4 H), 5.48 (s, 2 H); ¹³C NMR (CDCl₃) δ 20.05 (t, C-3, C-5), 20.35 (t, C-4), 23.11 (s, C-1), 31.14 (s, C-7), 52.13 (d, C-2, C-6), 127.49 (d, –CH=); HRMS calcd for C₁₆H₁₈⁷⁹Br₂ 367.97755, found 367.98]. The addition of iodine in ether to **7c** furnished a quantitative yield of **4** [mp 115 °C dec; ¹H NMR (CDCl₃) δ 1.15–1.68 (m, 4 H), 1.98–2.28 (m, 8 H), 3.15–3.63 (m, 4 H), 6.00 (s, 2 H); Anal. C, H]. The configuration at C-7 and C-7′ of **4** is assumed but is consistent with earlier observations on the addition of electrophiles to tricyclo[4.1.0.0²,⁷]heptanes.[6,7]

Reaction of **4** with 2.1 equiv of methyllithium in ether at –78 °C for 30 min followed by stirring the mixture for 30 min at 20 °C, and aqueous workup under nitrogen afforded a 94% yield of crystalline bis(propellane) **5** [mp 70–73 °C; ¹H NMR (C₆D₆) δ 0.90–1.70 (m, 12 H, 3-H₂, 4-H₂, 5-H₂), 2.13 (s, 2 H, 8-H), 2.50 and 4.10 (2 m, each 2 H, 2-H, 6-H, or reversed); ¹³C NMR (C₆D₆) δ 16.02 (s, C-1, C-7), 19.32 (t, C-4), 20.45 (t, C-3, C-5), 75.15 (d, C-8), 82.02 and 87.14 (2 d, C-2, C-6, or reversed); Anal. C, H]. An attempted distillation of **5** from a 100 °C bath/10⁻⁶ Torr led to polymeric material only. The structure of **5** was determined by X-ray diffraction[8] and is depicted in Figure 1.

The most important feature of the structure of **5** is the distance of the central [1.1.1]propellane C1–C7 bond which is 1.577 (1) Å. This is somewhat shorter than the corresponding CC bond in the parent hydrocarbon which, according to gas-phase electron diffraction measurements, was 1.594 Å,[9] and according to the analysis of its vibrational spectrum was determined to be 1.60 ± 0.02 Å.[10] The central bond in **5** is not significantly longer than the corresponding bond in a [3.1.1]propellane derivative, which was 1.574 Å.[11] The propellane side bonds of **5** (between 1.513

and 1.529 Å) compare well with the value of [1.1.1]propellane given in ref 9 (1.522 Å). The six angles of the three-membered rings at the bridgeheads C1 and C7 range from 58.30° to 59.24°; the three angles at C2, C6, and C8 are near 62.5°. The dihedral angles of the cyclopropane units are all close to 120°; the twist angle H1–C8–C8′–H1′ between the two C₈ subunits is 93.23°. At 1.494 Å, the C8–C8′ distance is somewhat shorter than in bicyclopropyl (1.517 ± 0.01 Å).[12]

The route to **5** could be generalized to a synthesis of eight-substituted tetracyclo[5.1.0.0¹,⁶.0²,⁷]octanes: Following the procedure from **6** to **7a** and from **7a** to **7c**, **8a** was obtained in 67% yield from **6** and 2-bromopropene and **8b** from **8a** in 55% yield.
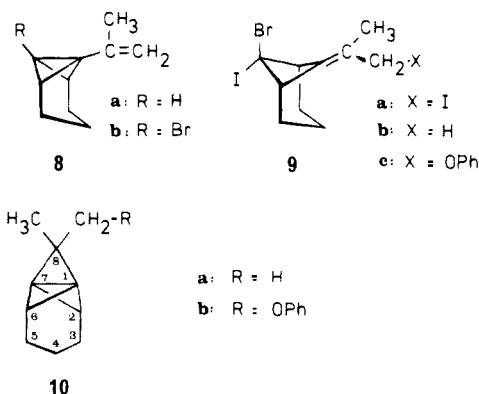
Addition of iodine to **8b** led essentially quantitatively to **9a**, which was reduced to **9b** with 3 equiv of LiAlH₄ in boiling ether in 79% yield or was converted into **9c** by reaction with potassium phenolate in acetone in 72% yield. Reductive cyclization of **9b** and **9c**, respectively, with methyllithium in ether at –78 °C afforded the propellanes **10a** and **10b** in yields of 57% and 95%. **10a**: ¹H NMR (C₆D₆) δ 1.05 (s, 6 H, CH₃), 1.05–1.75 (m, 6 H, 3-H₂, 4-H₂, 5-H₂), 3.48 (m, 2 H, 2-H, 6-H); ¹³C NMR (C₆D₆) δ 16.99 (q, CH₃), 19.26 (t, C-4), 19.26 (s, C-1, C-7), 20.99 (t, C-3, C-5), 79.87 (d, C-2, C-6), 83.86 (s, C-8). **10b**: ¹H NMR (C₆D₆) δ 1.08–1.70 (m, 6 H, 3-H₂, 4-H₂, 5-H₂), 1.20 (s, 3 H, CH₃), 3.48 (m, 2 H, 2-H, 6-H), 3.70 (s, 2 H, –CH₂-OPh), 6.65–7.18 (m, 5 H, Ph); ¹³C NMR (C₆D₆) δ 13.39 (q, CH₃), 19.11 (t, C-4), 19.48 (s, C-1, C-7), 20.72 and 20.84 (2 t, C-3, C-5, or reversed), 66.09

(5) For comparison, *trans*-**7b** was obtained by the Ni(0)-catalyzed coupling of 7-methyltricyclo[4.1.0.0²,⁷]hept-1-ylmagnesium bromide with *trans*-1-chloro-2-(1-tricyclo[4.1.0.0²,⁷]heptyl)ethylene. **7b** showed an olefinic coupling constant of 14.5 Hz. For stereochemical aspects of the Ni(0)-catalyzed coupling reaction, see: Tamao, K.; Zembayashi, M.; Kiso, Y.; Kumada, M. *J. Organomet. Chem.* **1973**, *55*, C91.

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(t, CH$_2$-OPh), 80.39 and 81.45 (2 d, C-2, C-6, or reversed), 86.57 (s, C-8), 114.9, 120.94, 129.55 (3 d, Ph), 159.56 (s, Ph).

Supplementary Material Available: Tables of positional parameters, bond distances, bond angles, and general displacement parameter expressions (U's) of 5 and experimental procedures for the preparation of 7a, 7c, 4, and 5 (4 pages). Ordering information is given on any current masthead page.

Neutron Spectroscopic Evidence for Adsorbed Hydroxyl Species on Platinum Black

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In recent years, there has been growing vibrational spectroscopic evidence for the existence of stable OH species adsorbed on single-crystal metal surfaces using electron energy loss spectroscopy (EELS). In particular, EEL spectra of OH species have been documented on Pt(111),[1] Pd(100),[2–4] Ag(110),[5] Ni(110),[6,7] and Rh(100)[8] surfaces. In contrast, there has been a scarcity of studies confirming the stability of OH species on high-surface-area metallic materials using other appropriate vibrational spectroscopic techniques. Morrow and Ramamurthy,[9] in one infrared (IR) study of some silica-supported group VIII metals, observed bands in the OH stretching region (430–460 meV) after the reaction of O$_2$ with hydrogen-covered Pt, Ir, Rh, Ni, Co, and Fe as well as after the reaction of H$_2$O with a partially reduced PtO surface.

In this paper, incoherent inelastic neutron scattering (IINS) was used to provide vibrational spectroscopic evidence for the formation of stable OH species adsorbed on an unsupported, microcrystalline, metal powder surface, namely, Pt black, in direct comparison with the reported EEL spectrum for OH/Pt(111).[1] The neutron's high sensitivity to vibrations involving hydrogen motions renders IINS a particularly useful technique for characterizing the vibrational spectra of hydrogenous adsorbates on high-surface-area materials.[10] Moreover, many IR-opaque materials, such as Pt black, are essentially neutron-transparent.

The Pt sample was prepared similar to previously described procedures.[11] Platinum black[12] (150 g) was washed in concentrated nitric acid at 295 K to remove residual potassium to less than 1 ppm (as measured by atomic absorption), rinsed in distilled water, loaded into a gold-sealed aluminum cell, and vacuum-dried at 373 K for 24 h. Surface oxygen was removed by saturating the sample with hydrogen[12] at 143 K, evacuating at 383 K for 24 h, reducing further in flowing H$_2$ at 383 K for 72 h, and finally

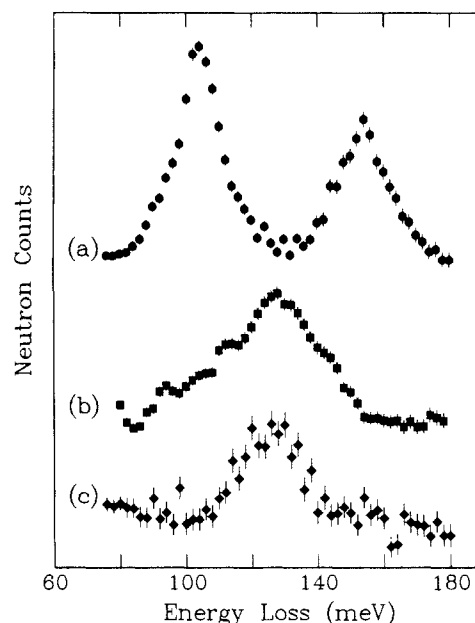

Figure 1. The IINS spectra (a) of residual hydrogen on Pt black, (b) after oxygen-titration of the residual hydrogen, and (c) after the addition of H$_2$ and O$_2$ to the oxygen-titrated surface (difference spectrum). See text for details. All spectra have been normalized to the same linear intensity scale.

evacuating at 383 K for >72 h. Hydrogen was initially introduced at such a low temperature to inhibit any particle sintering (i.e., surface-area reduction) due to localized heating from the exothermic formation of H$_2$O. The reduced sample (12-nm average crystallite size with 17 m^2 g^{-1} BET surface area) prepared in this fashion has been shown to possess approximately 0.4 monolayers of residual adsorbed hydrogen as evidenced by both deuterium isotope exchange and IINS intensity measurements.[11,13]

In an attempt to produce stable surface OH species, the residual hydrogen on the Pt black was titrated with O$_2$[12] (O:H ≈ 1) at 80 K, and the sample was annealed to 300 K over several hours and then recooled to 80 K. The 300 K annealment step was performed to ensure the homogeneous equilibration of H$_2$O and surface oxygen reaction products throughout the sample. The reported OH/Pt(111) results[1] have indicated that the 80 K recooling step should lead to the formation of stable surface OH species via the back reaction of the H$_2$O and surface oxygen. After spectral analysis, the oxygen-titrated Pt black surface was further dosed with H$_2$ at 80 K followed by an equivalent dose of O$_2$, enough to make an additional 0.5 monolayer of OH species. The sample was again annealed to 300 K over several hours and then recooled to 80 K for spectral analysis.

The IINS measurements were made at the National Bureau of Standards Research Reactor on the BT-4 Be-filter spectrometer with 40-min collimation before and after the Cu(220) monochromator. Energy resolution was a function of the incident energy: ca. 5–6 meV (1 meV = 8.065 cm^{-1}) below 90 meV and ca. 6% of the incident energy above 90 meV. All spectra were measured at 80 K and were corrected for fast-neutron background contributions where appropriate.

The IINS spectra are illustrated in Figure 1. The vibrational spectrum of the residual hydrogen on Pt black following the sample cleaning procedure, Figure 1a, indicates two scattering peaks maximized at 104 and 152 meV.[13] The assignment of these hydrogen modes is left for discussion in a subsequent paper.[14] The vibrational spectrum following the titration of the residual hydrogen with O$_2$, Figure 1b, indicates that the hydrogen scattering features have been replaced, for the most part, by a single band

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