were occasionally formed.[10] Stelzer reported the low yield preparation of $(iPr_2PCH_2CH_2CH_2)(iPr)PCH_2P(iPr)$-$(CH_2CH_2CH_2P\text{-}iPr_2)$, but this ligand has *not* been used to prepare any reported transition-metal dimer complexes.[11] We decided to use ethylene-linked terminal phosphines in LTTP because they simplify the synthetic procedure and give higher yields of the final tetratertiaryphosphine (88–92% yield based on Ph(H)PCH₂P-(H)Ph, 39–43% yield based on starting PPhH₂). The use of phenyl rings on the internal phosphines is another designed feature which should facilitate the crystallization of transition-metal dimer complexes for structural analyses. Although the all-phenyl-substituted LTTP ligand was prepared, our primary interest is in the ethyl-substituted LTTP (eLTTP) ligand because the electron rich alkylated terminal phosphines will coordinate strongly to transition-metal centers and be more effective at inhibiting dimer fragmentation processes (vide infra).

The reaction of eLTTP with $Rh_2(\mu\text{-}Cl)_2(CO)_4$ generates the golden-orange rhodium(I) eLTTP dimer $Rh_2Cl_2(CO)_2(eLTTP)$, 1.[12] An X-ray structure[13] on the material that crystallizes out of THF first reveals that the chiral *R,R*- and *S,S*-eLTTP diastereomer is present and has indeed coordinated to two Rh(I) centers. Parallel and perpendicular views of the dimer are shown in the ORTEP diagrams in Figure 1 with selected bond distances and angles listed in Table I. The dimer lies on a 2-fold rotation axis that passes through the central methylene bridge of the eLTTP ligand. The coordination geometry about the metal center is square planar with the expected distortions away from ideal due to the five-membered chelate ring. Surprisingly, not only is this the first reported crystal structure on two $MX(CO)(P_2)$ moieties linked together into a dimer complex, but it is also the first structurally characterized example of a $MX(CO)(P_2)$ (M = Rh, Ir; X = halide; P_2 = five-membered ring chelating bis-tertiaryphosphine) unit.

The $Rh_2(eLTTP)$ dimer adopts an open-mode conformation in which the two $RhCl(CO)P_2$ halves are symmetrically splayed apart by rotations about the central methylene bridge. The Rh–Rh separation is 5.813 (2) Å with a Rh–P1···P1′–Rh′ torsional angle of 123°. This open-mode orientation is similar to those seen for

some eHTP binuclear systems which have symmetrically splayed M1–P···P–M2 torsional angles ranging from 58° to 102°.[3,5] A major difference, however, is that the central P–CH₂–P angle of 113 (1)° for $Rh_2Cl_2(CO)_2(eLTTP)$ is markedly smaller than those observed for related $M_2Cl_2(eHTP)^{2+}$ systems which range from 126.6 (4)° for $Pd_2Cl_2(eHTP)^{2+}$ to 129.7 (9)° for Pt_2Cl_2-$(eHTP)^{2+}$.[3,14] This unquestionably points to significantly reduced steric interactions between each half of the eLTTP ligand system and strongly suggests that rotations about the central methylene bridge should be facile and could allow the metal centers to interact or cooperate in the activation or reaction of a substrate.

The difference between the stabilities of 1 and the somewhat related dimer $Rh_2(\eta^4\text{-}COD)_2(tetraphos)$ is demonstrated by the fact that the tetraphos-based Rh(I) dimer reacts with H₂ under *ambient* conditions to *readily* fragment to the mononuclear species $Rh(\eta^4\text{-tetraphos})^+$.[10e] $Rh_2Cl_2(CO)_2(eLTTP)$, in marked contrast, shows no signs of fragmentation even under considerably more rigorous conditions (50 bar H₂/CO, 80 °C). The catalytic activity of mononuclear $MX(CO)P_2$ (M = Rh, Ir) species is well studied, and it will be most interesting to see if the metal centers in this unique eLTTP bridged dimer system can cooperate to produce novel reactivities.

Supplementary Material Available: Tables of crystal and structure refinement parameters, positional parameters, anisotropic thermal parameters, and full bond distances and angles (4 pages); a listing of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

(10) (a) Butler, I. S.; Coville, N. J. *J. Organomet. Chem.* **1974**, *66*, 111. (b) Khan, M. M. T.; Mohiuddin, R. *J. Coord. Chem.* **1977**, *6*, 171. (c) Arcken, U. P.; Rehder, D. *J. Organomet. Chem.* **1980**, *185*, 219. (d) Khan, M. M. T.; Ahamad, S. S.; Ahmed, M. *J. Inorg. Nucl. Chem* **1980**, *42*, 547. (e) Brown, J. M.; Canning, L. R. *J. Organomet. Chem.* **1984**, *267*, 179.
(11) Hietkamp, S.; Sommer, H.; Stelzer, O. *Chem. Ber.* **1984**, *117*, 3414.
(12) eLTTP (0.235 g, 0.51 mmol) in 25 mL of THF is gradually added via a cannula to 0.197 g (0.51 mmol) of $Rh_2(\mu\text{-}Cl)_2(CO)_4$ in 25 mL of THF in a dry ice/acetone bath under inert atmosphere conditions. The yellow Rh solution turns a golden-red color after the first drop of eLTTP, and the solution was occasionally flushed with N₂ to remove any CO released from the reaction which was allowed to gradually warm to room temperature and left to stir overnight. A small amount (0.06 g) of an unidentified red-brown precipitate was separated by filtration, and the red-orange filtrate vacuum evaporated to dryness. The orange-red solid was redissolved in ca. 20 mL of THF which deposited small X-ray quality orange-red crystals of a uniform morphology of the racemic chiral-eLTTP diastereomer upon slow evaporation of solvent. Total isolated yield of $Rh_2Cl_2(CO)_2(eLTTP)$, 40–47%; isolated crystalline yield of *chiral*-$Rh_2Cl_2(CO)_2(eLTTP)$, 15–20%. Spectroscopic data on the structurally characterized *chiral*-$Rh_2Cl_2(CO)_2(eLTTP)$: IR (KBr, ν_{CO}) 1970 cm⁻¹; ³¹P{¹H} NMR (CD₂Cl₂, ppm, H₃PO₄ reference) 77.65 (dd, 1 P, external phosphorus atom, J_{P-P} = 31.3 Hz, J_{Rh-P} = 148.9 Hz), 48.65 (m, 1 P, internal phosphorus atom, J_{Rh-P} = 139.3 Hz). Satisfactory analytical data (C, H) was obtained on toluene recrystallized samples of 1 (Oneida Research Services, Whitesboro, NY.).
(13) Crystallizes in the monoclinic space group *P2/c* with the following unit cell parameters: a = 13.419 (3) Å, b = 9.361 (2) Å, c = 15.574 (6) Å, β = 102.62 (3)°, V = 1909 (1) Å³, Z = 2. Data were collected on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation, and an empirical absorption correction was performed. The structure was refined by using the Enraf-Nonius SDP program set to give final discrepancy indices of R = 0.048 and R_w = 0.062 with a GOF = 1.15 based on 989 unique data with $F_o^2 > 3\sigma(F_o^2)$. The terminal ethyl groups on the eLTTP ligand were disordered and successfully modeled and refined with isotropic thermal parameters; a disordered THF solvent molecule lying on the 2-fold axis could not, however, be modeled, and an unusually large anisotropic thermal parameter for the THF oxygen atom resulted. The data set was limited due to the small size of the crystal and its less than ideal diffraction characteristics. Tables of X-ray data collection and structure solving parameters, positional parameters, anisotropic thermal parameters, full bond distances and angles, and observed and calculated structure factors are included in the Supplementary Material.

(14) Saum, S. E.; Laneman, S. A.; Stanley, G. G. *Inorg. Chem.*, submitted for publication.

An "Expanded Porphyrin": The Synthesis and Structure of a New Aromatic Pentadentate Ligand

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The porphyrins and related tetrapyrrole macrocycles are among the most versatile of *tetradentate* ligands.[1] Attempts to stabilize higher coordination geometries, however, with larger porphyrin-like aromatic macrocycles have met with little success.[2-5] Indeed, to date, only the uranyl complex of "superphthalocyanine" has

(1) *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978–1979; Vols. I–VII.
(2) "Superphthalocyanine", a pentaaza aromatic phthalocyanine-like system was prepared by a uranyl-mediated condensation; it is not obtainable as the free-base or in other metal-containing forms: (a) Day, V. W.; Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc.* **1975**, *97*, 4519–4527. (b) Marks, T. J.; Stojakovic, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 1695–1705. (c) Cuellar, E. A.; Marks, T. J. *Inorg. Chem.* **1981**, *208*, 3766–3770.
(3) Bauer, V. J.; Clive, D. R.; Dolphin, D.; Paine, J. B. III; Harris, F. L.; King, M. M.; Loder, J.; Wang, S.-W. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 6429–6436. To date only tetracoordinated metal complexes have been prepared from these potentially pentadentate ligands.
(4) For an interesting example of a porphyrin-like system with a smaller central cavity, see: (a) Vogel, E.; Kocher, M.; Schmickler, H.; Lex, J. *Angew. Chem.* **1986**, *98*, 262–263; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 257–258. (b) Vogel, E.; Balci, M.; Pramod, K.; Koch, P.; Lex, J.; Ermer, O. *Angew. Chem.* **1987**, *99*, 909–912; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 928–931.
(5) Mertes et al. have recently characterized a five-coordinate copper complex of an elegant (but nonaromatic) porphyrin-like "accordion" ligand derived from dipyrromethines: (a) Acholla, F. V.; Mertes, K. B. *Tetrahedron Lett.* **1984**, 3269–3270. (b) Acholla, F. V.; Takusagawa, F.; Mertes, K. B. *J. Am. Chem. Soc.* **1985**, 6902–6908. Four-coordinate copper complexes of other *nonaromatic* pyrrole-containing macrocycles have also been prepared recently: Adams, H.; Bailey, N. A.; Fenton, D. A.; Moss, S.; Rodriguez de Barbarin, C. O.; Jones, G. *J. Chem. Soc., Dalton Trans.* **1986**, 693–699.

been isolated and characterized structurally,[2] although several other large porphyrin-like aromatic macrocycles, including the "sapphyrins",[3,6] "oxosapphyrins",[6,7] "platyrins",[8] "pentaphyrin",[9] and "[26]porphyrin",[10] have been prepared in their metal-free forms. We therefore sought to develop a new type of "expanded porphyrin" capable of binding a variety of metal cations and present here the synthesis of **2**,[11] an unprecedented porphyrin-like aromatic *pentadentate* ligand,[2,12] and the structure of its cadmium(II) bispyridine complex **4**.

1

2 M = H, n = 0
3 M = Cd, n = 1
4 M = Cd, n = 1, L = pyr
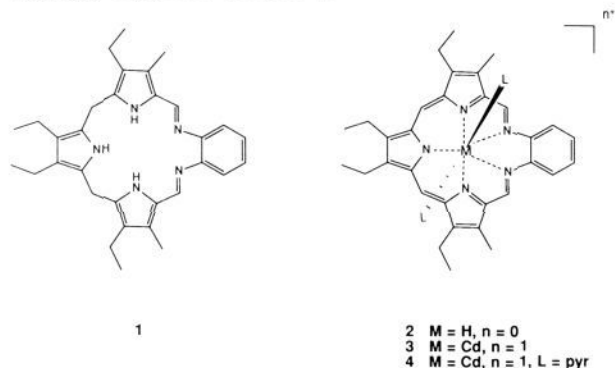
We have recently prepared the nonaromatic methylene-bridged macrocycle **1** by the direct acid-catalyzed condensation of 2,5-bis[3-ethyl-5-formyl-4-methylpyrrol-2-yl)methyl]-3,4-diethyl-pyrrole and *o*-phenylenediamine[13] and determined it to be an ineffective cheland.[14] We have now found that stirring the reduced macrocycle **1** with cadmium chloride for 24 h in chloroform–methanol (1:2 v.v.) in the presence of air, followed by chromatographic purification on silica gel and recrystallization from chloroform–hexanes, gives the cadmium(II) complex **3·Cl** in 24% yield as a dark green powder.[15] Under the reaction conditions both ligand oxidation and metal complexation take place spontaneously.

The structure of **3** suggests that it can be formulated as either an 18 π-electron benzannelated [18]annulene or as an overall 22 π-electron system; in either case an aromatic structure is defined. The proton NMR spectrum of **3·Cl** is consistent with the proposed aromaticity. For the most part, complex **3·Cl** shows ligand features which are qualitatively similar to those observed for **1**. As would be expected in the presence of a strong diamagnetic ring current, however, the alkyl, imine, and aromatic peaks are all shifted to lower field. Furthermore, the bridging methylene signals of **1** (at $\delta \simeq 4.0$)[13] are replaced by a sharp singlet, at 11.3 ppm, ascribable

(6) Broadhurst, M. J.; Grigg, R.; Johnson, A. W. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2111–2116.

(7) (a) Broadhurst, M. J.; Grigg, R.; Johnson, A. W. *J. Chem. Soc., Chem. Commun.* **1969**, 23–24. Broadhurst, M. J.; Grigg, R.; Johnson, A. W. *J. Chem. Soc., Chem. Commun.* **1969**, 1480–1482. Broadhurst, M. J.; Grigg, R.; Johnson, A. W. *J. Chem. Soc., Chem. Commun.* **1970**, 807–809.

(8) (a) Berger, R. A.; LeGoff, E. *Tetrahedron Lett.* **1978**, 4225–4228. (b) LeGoff, E.; Weaver, O. G. *J. Org. Chem.* **1987**, 710–711.

(9) (a) Rexhausen, H.; Gossauer, A. *J. Chem. Soc., Chem. Commun.* **1983**, 275. (b) Gossauer, A. *Bull. Soc. Chim. Belg.* **1983**, 92, 793–795.

(10) Gosmann, M.; Franck, B. *Angew. Chem.* **1986**, 98, 1107–1108; *Angew. Chem., Int. Ed. Engl.* **1986**, 25, 1100–1101.

(11) The systematic name for compounds **2** is 4,5,9,24-tetraethyl-10,23-dimethyl-13,20,25,26,27-pentaazapentacyclo[20.2.1.1[3,6].1[8,11].0[14,19]]heptacosa-1,3,5,7,9,11(27),12,14,16,18,20,22(25),23-tridecaene.

(12) Nonaromatic planar pentadentate pyridine-derived ligands are known. See, for instance: (a) Curtis, N. F. In *Coordination Chemistry of Macrocyclic Compounds*; Melson, G. A., Ed.; Plenum: New York, 1979; Chapter 4. (b) Nelson, S. M. *Pure Appl. Chem.* **1980**, 52, 2461–2476. (c) Ansell, C. W. G.; Lewis, J.; Raithby, P. R.; Ramsden, J. N.; Schroder, M. *J. Chem. Soc., Chem. Commun.* **1982**, 546–547. (d) Lewis, J.; O'Donoghue, T. D.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 1383–1389. (e) Constable, E. C.; Chung, L.-Y.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1986**, 1719–1720. (f) Constable, E. C.; Holmes, J. M.; McQueen, R. C. S. *J. Chem. Soc., Dalton Trans.* **1987**, 5–8.

(13) Sessler, J. L.; Johnson, M. R.; Lynch, V. *J. Org. Chem.* **1987**, 52, 4394–4397.

(14) Sessler, J. L.; Johnson, M. R.; Lynch, V.; Murai, T. *J. Coord. Chem.*, in press.

(15) Satisfactory spectroscopic, mass spectrometric, and/or analytical data were obtained for all new compounds (see Supplementary Material).
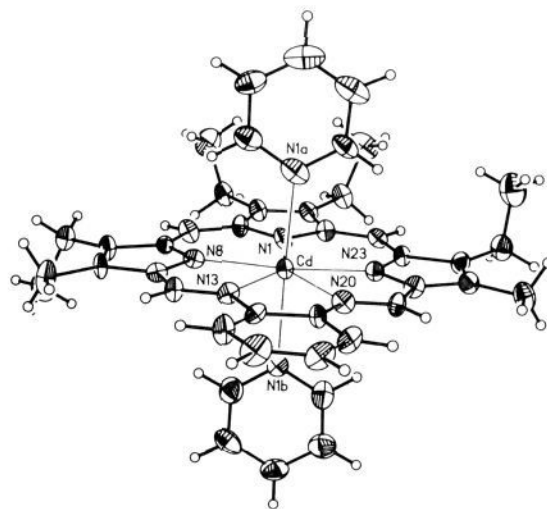

Figure 1. View of **4** showing coordination to Cd. Ellipsoids scaled to the 40% probability level. The Cd ion lies in the plane of the nearly planar macrocycle (maximum deviation from planarity 0.10 (1) Å). Relevant Cd–N bond lengths (Å) are as follows: 2.418 (7), N1; 2.268 (8), N8; 2.505 (7), N13; 2.521 (7), N20; 2.248 (8), N23; 2.438 (14), N1a; 2.473 (12), N1b. Selected N–Cd–N bond angles (deg) are as follows: N1–Cd–N8, 78.9 (2); N1–Cd–N23, 80.2 (3); N8–Cd–N13, 68.4 (2); N13–Cd–N20, 64.4 (2); N20–Cd–N23, 68.2 (3); N1a–Cd–N1b, 176.1 (4).
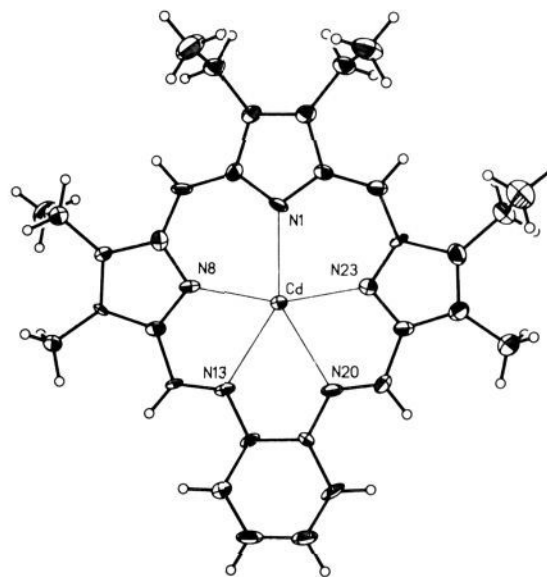

Figure 2. View of **4** perpendicular to the plane through the macrocycle. Pyridine rings (not shown) lie perpendicular to the macrocycle with dihedral angles of 88.5 (4)° for ring a and 89.1 (3)° for ring b.

to the bridging methine protons. The chemical shift of this "meso" signal is greater than that observed for Cd(OEP)[16] ($\delta \simeq 10.0$),[17] an appropriate 18 π-electron aromatic reference system, and is quite similar to that observed for the free-base form of deca-methylsapphyrin ($\delta \simeq 11.5$–11.7),[3] a 22 π-electron pyrrole-containing macrocycle.

The optical spectrum of **3·Cl** bears some resemblance to those of other aromatic pyrrole-containing macrocycles[3,6,7,18] and provides further support for the proposed aromatic structure. The dominant transition is a Soret-like band at 424 nm ($\epsilon = 72\,700$), which is considerably less intense than that seen for Cd(OEP)(pyr)[16] (λ_{max}

(16) OEP = octaethylporphyrin and TPP = tetraphenylporphyrin; the prefixes H$_2$ and Cd refer to the free-base and cadmium(II) forms, respectively; pyr = pyridine.

(17) (a) Scheer, H.; Katz, J. J. In *Porphyrins and Metalloporphyrins*; Smith, K., Ed.; Elsevier: Amersterdam, 1975; Chapter 10. (b) Janson, T. R.; Katz, J. J.; in ref 1, Vol IV, Chapter 1.

= 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·NO$_3$·(HNO$_3$). Upon treatment with excess pyridine and recrystallization from chloroform–hexane, the bis-pyridine adduct 4·NO$_3$, with spectral properties essentially identical with 3·Cl, was isolated as dark green crystals.[15] The molecular structure of 4·NO$_3$, 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·NO$_3$ the cadmium atom is *seven-coordinate*, being complexed by *two apical pyridine ligands*. The configuration about the Cd atom is thus *pentagonal bipyridimal*; 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$_2$S 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 sp^3-linked macrocycle, octaethylporphyrinogen (δ(NH) = 6.9),[27] is oxidized to the corresponding porphyrin, H$_2$OEP (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, ^{1}H NMR and UV–vis spectra for 2 and 3·Cl, atom labeling scheme for 4, X-ray experimental data for 4·NO$_3$, 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.

(18) Gouterman, M., in ref 1, Vol. III, Chapter 1.

(19) Becker, R. S.; Allison, J. B. *J. Phys. Chem.* **1963**, *67*, 2669.

(20) Crystal data: 4·NO$_3$ crystallized from CHCl$_3$–hexanes in the triclinic space group, $P\bar{1}$ (no. 1), with a = 9.650 (3) Å, b = 10.217 (4) Å, c = 11.295 (4) Å, α = 98.16 (3), β = 107.05 (2), γ = 92.62 (3)°, V = 1049.3 (6) Å^3, and ρ_c = 1.49 g·cm^{-3} for Z = 1. Unique reflections (5654) (4936 with $F \geq 6\sigma(F)$) using ω scans were collected at 193 K on a Nicolet R3m/V with Mo Kα radiation (λ = 0.71069 Å) out to 2θ of 50°. Data corrected for decay, Lp effects, and absorption. Refined by conventional means to an R = 0.0534. All non-H atoms refined anisotropically. H atom positions calculated (d_{C-H} 0.96 Å) and refined isotropically riding on the relevant C atom. The non-coordinated nitrate ion is within H-bonding distance of the CHCl$_3$ solvent molecule with O···C (CHCl$_3$) and O···H distances of 3.00 (2) Å and 2.46 (2) Å, respectively. For full details see Supplementary Material.

(21) Hoard, J. L., in ref 17a, Chapter 8.

(22) Hazell, A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 296–299.

(23) Rodesiler, P. F.; Griffith, E. H.; Ellis, P. D.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1980**, 492–493.

(24) (a) Miller, J. R.; Dorough, G. D. *J. Am. Chem. Soc.* **1952**, *74*, 3977–3981. (b) Kirksey, C. H.; Hambright, P. *Inorg. Chem.* **1970**, *9*, 958–960.

(25) Compound 4 appears to be the first seven-coordinate cadmium complex derived from all nitrogen donors. For examples of other pentagonal bipyramidal cadmium complexes, see: (a) Cameron, A. F.; Taylor, D. W.; Nuttall, R. H. *J. Chem. Soc., Dalton Trans.* **1972**, 1608–1614. (b) Liles, D. C.; McPartlin, M.; Tasker, P. A.; Lip, H. C.; Lindoy, L. F. *J. Chem. Soc., Chem. Commun.* **1976**, 549–551. (c) Nelson, S. M.; McFall, S. G.; Drew, M. G. B.; Othman, A. H. B.; Mason, N. G. *J. Chem. Soc., Chem. Commun.* **1977**, 167–168. (d) Drew, M. G. B.; Othman, A. H. B.; McFall, S. G.; McIlroy, A. D. A.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1173–1180. (e) Charles, N. G.; Griffith, E. A. H.; Rodesiler, P. F.; Amma, E. L. *Inorg. Chem.* **1983**, *22*, 2717–2723.

(26) Other oxidants, including DDQ, Ag$_2$O, I$_2$, PtO$_2$, PbO$_2$, SeO$_2$, and Ph$_3$CBF$_4$, either failed to react or gave rise only to decomposition products.

(27) Whitlock, H. W., Jr.; Buchanan, D. H. *Tetrahedron Lett.* **1969**, *42*, 3711–3714.

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] [^{1}H NMR (CDCl$_3$) δ 1.38 (m, 14 H), 2.70 (m, 4 H), 5.38 (s, 2 H); ^{13}C NMR (CDCl$_3$) 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 ^{1}H NMR spectroscopy after introduction of a methyl group at C-7 giving 7b which showed

(1) Belzner, J.; Szeimies, G. *Tetrahedron Lett.* **1987**, 3099. In addition, 1 was obtained from 3,3-dibromomethylenecyclobutane (3, X = Br) and methyllithium in 76% yield. Fuchs, J.; Szeimies, G., unpublished.

(2) Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669, and references therein. See, also: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Application of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 14.

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

(4) Experimental procedures are included as Supplementary Material.