centered icosahedral structure has long been observed in main-group clusters such as $[B_{12}H_{12}]^{2-}$[15] or its analogues[16] and a number of carboranes and metallacarboranes.[17] Transition-metal clusters, on the other hand, can have *centered* icosahedral or bpp cages as exemplified by $[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+}$[18] and $[Pt_{19}(CO)_{22}]^{4-}$,[19] respectively. Mixed transition-metal/main-group clusters can adopt either *noncentered* (as in $[Ni_{10}(AsMe)_2(CO)_{18}]^{2-}$[20] as well as in metallacarboranes[17]) or *centered* (as in $[Ni_{11}(SnMe)_2(CO)_{18}]^{2-}$[21]) structures. In this respect, clusters **1** and **2** may be considered as the *centered* analogues of the vertex-sharing *noncentered* icosahedral metallacarborane clusters as exemplified by $[M(C_2B_9H_{11})_2]^{n-4}$ where $M^{n+} = Fe^{2+}, Co^{3+}, Ni^{4+}$.[22]

It occurs to us that the ses metal configuration observed in **2** signifies the genesis of a "polyicosahedral" *growth pathway* via vertex sharing to give bi-, tri-, and tetraicosahedral supraclusters as exemplified by the 25-metal-atom (this work), 37-metal-atom $[(p\text{-}Tol_3P)_{12}Au_{18}Ag_{19}Br_{11}]^{2+}$[6] or 38-metal-atom $[(p\text{-}Tol_3P)_{12}Au_{18}Ag_{20}Cl_{14}]$,[7] and 46-metal-atom $[(Ph_3P)_{12}Au_{24}Ag_{22}Cl_{10}]$[8] supraclusters. In all these known structures, the icosahedral units are linked by (interpenetrating) bicapped pentagonal prisms (as in the ses configuration), instead of (interpenetrating) icosahedra (as in the sss configuration).

Acknowledgment is made to the National Science Foundation (CHE-8722339) for financial support of this research.

Supplementary Material Available: Full listings of complete structural data (Table A), positional parameters (Table B), interatomic distances (Table C), interatomic angles (Table D), and anisotropic thermal parameters (Table E) and preparation and crystallization (Table G) for the title compound (26 pages); full listing of observed and calculated structure factors for the title compound (Table F) (69 pages). Ordering information is given on any current masthead page.

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Dicycloproparenes

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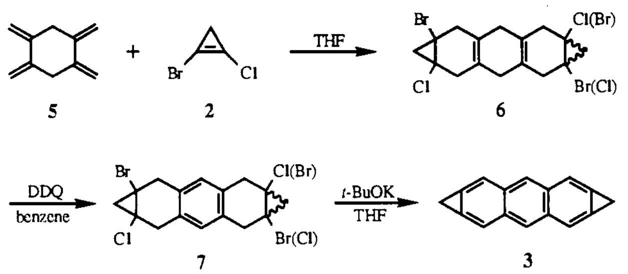
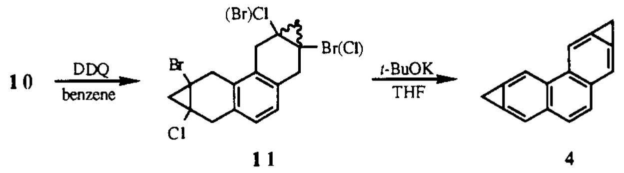
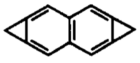
Although benzocyclopropene[2] and its derivatives[3] have become readily available since the report by Anet and Anet[4] describing the synthesis of the first member of this family, the only dicycloproparene that has been reported is the thermally sensitive dicyclopropanaphthalene **1**.[5] We report here the utilization of the cycloproparene synthon 1-bromo-2-chlorocyclopropene (**2**)[6] in the preparation of the novel dicycloproparenes **3**[7] and **4** and some of their derivatives.

Scheme I



Scheme II

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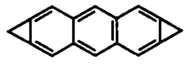
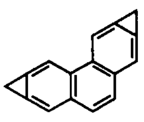

3


4

The synthetic route to 1*H*,5*H*-dicycloprop[*b*,*i*]anthracene (**3**) is illustrated in Scheme I. Addition of an 8-fold excess of **2**[8] to tetraene **5**[9] in THF at -20 °C for 7 days gave the adduct **6**[10,11] in 80% yield. Treatment of **6** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in benzene at 50–60 °C for 10 h followed by chromatography afforded **7** in 93% yield. Conversion to **3** was effected by treatment of **7** with potassium *tert*-butoxide in THF at -20 °C for 1 h, providing nearly pure **3** as a fine white solid, mp 127–128 °C dec, in 38% yield after chromatography.

The ^1H NMR spectrum of **3** displays the expected pattern with singlets at δ 3.58 ppm (CH_2), 7.69 (H_2, H_4, H_6, H_8), and 8.45 (H_3, H_7). The ^{13}C NMR spectrum (75.5 MHz) shows signals at δ 18.8 (C_1, C_5), 111.5 (C_2, C_4, C_6, C_8), 123.0 (C_{1a}, C_{4a}, C_{5a}, C_{8a}), 126.8 (C_3, C_7), and 134.8 (C_{2a}, C_{3a}, C_{6a}, C_{7a}). The UV spectrum (pentane) exhibits a maximum at 256 nm (ϵ 35 500) with other absorptions at 332, 348, and 364 nm. The infrared

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(1) American Chemical Society, Division of Organic Chemistry Fellow, 1990–1991, sponsored by the Rohmand Haas Company.

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(7) For an interesting discussion on the anticipated properties of **3**, see: Davalian, D.; Garratt, P. J.; Koller, W.; Mansuri, M. M. *J. Org. Chem.* **1980**, *45*, 4183.

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(9) Longone, D. T.; Boettcher, F.-P. *J. Am. Chem. Soc.* **1963**, *85*, 3436. Longone, D. T.; Warren, C. L. *J. Am. Chem. Soc.* **1962**, *84*, 1507. See also: Bailey, W. J.; Fetter, E. J.; Economy, J. E. *J. Org. Chem.* **1962**, *27*, 3479. Surprisingly, our work represents the first use of **5** in synthesis.

(10) Spectral data and physical constants for new cycloproparenes are as follows. **4**: mp 85–86 °C; ^1H NMR δ 8.64 (d, $J = 1.6$, 2 H), 7.84 (s, 2 H), 7.70 (d, $J = 1.6$, 2 H), 3.59 (s, 4 H); ^{13}C NMR δ 135.0, 134.0, 126.9, 124.8, 123.9, 113.9, 108.3, 19.4; IR 1670 cm^{-1}; UV λ_{max} 250 nm (ϵ 14 500), 282 (8700), 294 (6050), 323 (600); HRMS calcd for $C_{16}H_{10}$ *m/e* 202.0783, found 202.0782. Anal. Calcd: C, 95.02; H, 4.98. Found: C, 94.97; H, 5.05. **12**: pale yellow oil; ^1H NMR δ 7.53 (s, 2 H), 5.55 (s, 2 H), 5.00 (s, 2 H), 3.26 (s, 2 H), 2.63 (s, 4 H); ^{13}C NMR δ 144.5, 136.7, 126.2, 111.2, 108.6, 34.0, 19.2; IR 1655, 1620 cm^{-1}; UV λ_{max} 246 nm (ϵ 5350), 276 (4630), 313 (800); HRMS for $C_{13}H_{12}$ calcd 168.0939, found 168.0942. **13**: mp 125 °C dec; ^1H NMR δ 7.22 (s, 4 H), 4.00 (s, 4 H), 3.29 (s, 4 H); ^{13}C NMR δ 138.9, 124.7, 114.3, 38.0, 20.6; IR 1670 cm^{-1}; UV (pentane) λ_{max} 259 nm (ϵ 1690), 282 (4120), 288 (4010); HRMS calcd for $C_{16}H_{12}$ *m/e* 204.0939, found 204.0941. Anal. Calcd: C, 94.08; H, 5.92. Found: C, 94.14; H, 5.94. **14**: mp 53–54 °C; ^1H NMR δ 7.71 (d, 2 H, $J = 1.5$), 7.20 (d, 2 H, $J = 1.5$), 3.33 (s, 4 H), 2.92 (s, 4 H); ^{13}C NMR δ 139.9, 137.2, 125.4, 125.3, 115.0, 111.5, 30.4, 19.9; IR 1665 cm^{-1}; UV λ_{max} 254 nm (ϵ 1900), 285 (5400), 296 (4700); HRMS calcd for $C_{16}H_{12}$ *m/e* 204.0939, found 204.0938. Anal. Calcd: C, 94.08; H, 5.92. Found: C, 94.05; H, 5.88.

(11) Although the cycloadditions employed to give **6**, **10**, and **16** yield products of unknown stereochemistry, we have not found any evidence that the subsequent reactions are affected by the stereochemistry of the starting material.

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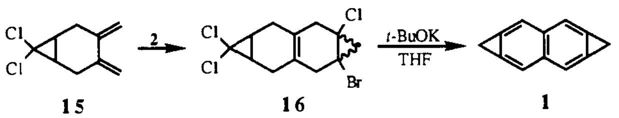
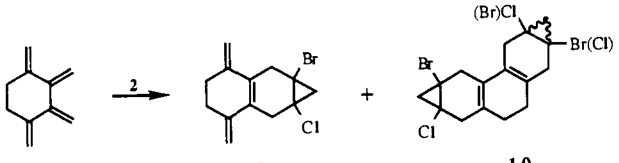
Scheme III



15 16 1

spectrum showed the characteristic benzene "double bond" at 1660 cm^{-1}. Elemental composition was provided by combustion analysis. Calcd for $C_{16}H_{10}$: C, 95.02; H, 4.98. Found: C, 94.95; H, 5.04.

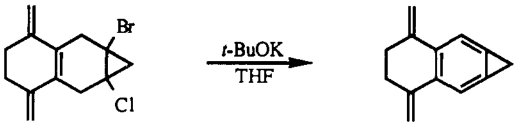
The starting material required for the synthesis of 1*H*,4*H*-dicyclopropa[*b*,*h*]phenanthrene (**4**) can be prepared from the reactive tetraene **8**.[12] Thus treatment of **8** with a 6-fold excess of **2** for 5 days at −20 °C gave adduct **9** (55% yield) along with the desired bis-adduct **10** (10% yield).



8 9 10

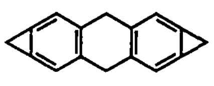
After separation by column chromatography, **10** was aromatized with DDQ in benzene at 65 °C for 18 h to yield **11** in 64% yield (Scheme II). Reaction of **11** with potassium *tert*-butoxide in THF provided **4**, mp 85–86 °C, in 84% yield after chromatography.

The interesting cyclopropa[*b*]naphthalene derivative **12** could be isolated in 57% yield when **9** was treated with potassium *tert*-butoxide. Surprisingly, the *tert*-butoxide/THF medium used to effect the elimination of **9** does not induce a base-catalyzed prototropic rearrangement of the double bonds in **12**.

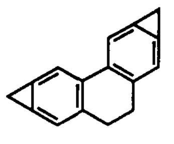


9 12

Treatment of **6** and **10** with potassium *tert*-butoxide in THF provided the dihydro derivatives **13** and **14** in 31% and 77% yields, respectively.[13]



13



14

Finally, this route can also be used as an alternative synthesis of **1** (Scheme III). Reaction of **2** with Garratt's diene (**15**)[7] yielded the cycloadduct **16** (42% yield), which could be converted readily into **1** (52% yield).

We are currently pursuing the preparation of other di- and tricycloproparenes. Results of these studies will be reported later.

Acknowledgment. We gratefully acknowledge the Robert A. Welch Foundation for support of this work. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We thank Scott Flanagan for the elemental analyses.

Supplementary Material Available: Experimental procedures for the syntheses of **1–14** and **16** including complete spectral characterization (3 pages). Ordering information is given on any current masthead page.

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(12) Hopf, H.; Gottschild, D.; Lenk, W. *Isr. J. Chem.* **1985**, *26*, 79. To the best of our knowledge, **8** has not been used previously in synthesis.

(13) These dicycloproparenes as well as **3** and **4** are surprisingly stable compounds, decomposing only slowly at −20 °C after several weeks.

Binuclear Palladium Complexes with Bridging Hydrides. Unusual Coordination Behavior of $LiBEt_4$

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Metal hydrides constitute an important class of molecules that have relevance to catalysis, organic synthesis, and hydrogen storage.[1] Although soluble metal hydride complexes are known for most of the transition elements, palladium derivatives containing hydride ligands are relatively rare.[2] This is particularly surprising since homogeneous catalysis by palladium complexes is well-known and in many cases participation by a palladium hydride[3] species is inferred. A number of square-planar derivatives of the formula *trans*-$PdH(X)(PR_3)_2$ have been prepared and characterized;[4] however, no examples of palladium dimers having bridging hydrides have been as yet unequivocally characterized.[5]

Our interest in the reactivity of binuclear hydride-bridged complexes[6] was incentive enough to examine the preparation of the noticeably absent palladium analogues of certain nickel and platinum dimers[7] of the formula $[P_2M]_2(\mu\text{-}H)_2$ where M = Ni or Pt and P_2 is bidentate phosphine. In this report the preparation of the first structurally characterized hydride-bridged dimer of palladium is described. An unexpected bonus in this work was the discovery that the dimer also has a $LiBEt_4$ molecule as part of the structure.

Addition of 2 equiv of a stock THF solution of $LiBEt_3H$ (Aldrich Super-Hydride) to a THF slurry of (dippp)$PdCl_2$ (dippp = 1,3-bis(diisopropylphosphino)propane) at −40 °C led to the formation of a deep red solution, from which red crystals of the formula $(dippp)_2Pd_2H_2\cdot LiBEt_4$ (**1**) could be isolated in approximately 68% yield[8] as shown in Scheme I.

The X-ray crystal structure[9] of **1** is also shown in Scheme I. The binuclear structure is clearly evident as are the bridging

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[†] E. W. R. Steacie Fellow, 1990–1992.

[‡] NSERC of Canada Postdoctoral Fellow, 1988–1990.

[§] Killam Postgraduate Scholar, 1989–1990.

[∥] Professional Officer: UBC Crystallographic Service.

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(4) See, for example: (a) Brooks, E. H.; Glockling, F. *J. Chem. Soc. A* **1967**, 1030. (b) Munakata, H.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1970**, 881. (c) Di Bugno, C.; Pasquali, M.; Leoni, P.; Sabatino, P.; Braga, D. *Inorg. Chem.* **1989**, *28*, 1390.

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(8) ^1H NMR (ppm, C_6D_6): δ 1.78 (br m, 6 H), 1.29 (m, 10 H), 1.20 and 1.07 (m, 24 H), 0.42 (br m, 4 H), −3.66 (br quin, 1 H). $^{31}P\{^1H\}$ NMR (ppm, C_6D_6): δ 22.4 (br s). Anal. Calcd for $C_{38}H_{90}BLiP_4Pd_2$ (found): C, 50.62 (50.57); H, 10.06 (10.06).

(9) Crystals of $[(dippp)Pd]_2(\mu\text{-}H)_2\cdot LiBEt_4\cdot 0.5(C_6H_{14})$ are monoclinic, $a = 11.531$ (2) Å, $b = 19.105$ (4) Å, $c = 24.002$ (4) Å, $\beta = 98.64$ (2)°, $Z = 4$, $D_{calcd} = 1.200$ g cm^{-3}, space group $P2_1/n$. The structure was solved by the Patterson method and was refined by full-matrix least-squares procedures to $R = 0.033$ and $R_w = 0.037$ for 5948 reflections with $I \geq 3\sigma(I)$. Full details of the crystallographic analysis are included as supplementary material.

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