first well-characterized example of a homogeneous reaction of methane with an organometallic complex: the exchange of $^{13}CH_4$ with $(\eta\text{-}C_5Me_5)_2MCH_3$ (M = Lu, Y). In the mechanism proposed,[20] oxidative addition of C–H to Lu(III) was considered unlikely, since it would require a Lu(V) intermediate. In this respect, the reactions of methane with the lutetium or yttrium systems appear to differ from those of iridium reported here. We are aware of no prior report of the oxidative addition of methane to a metal complex in which the product was characterized.[21]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for financial support.

Registry No. 1, 32660-96-1; **2a**, 87739-20-6; **2b**, 87739-21-7; **3a**, 87739-22-8; **3b**, 87739-23-9; $(\eta^5\text{-}C_5H_5)Ir(CO)_2$, 12192-96-0; methane, 74-82-8.

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(20) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491–6493. We thank Dr. Watson for informing us of her results prior to publication.

(21) After the submission of this manuscript, we learned that R. G. Bergman and co-workers had succeeded in thermally activating methane to form $(\eta\text{-}C_5Me_5)Ir(PMe_3)(H)CH_3$, a complex closely related to **2a**. cf.: *Chem. Eng. News*, **1983**, *61*, 33–36 (Sept 12, No. 37).

Dicycloocta[1,2,3,4-*def*:1′,2′,3′,4′-*jkl*]biphenylene. Benzenoid Atropism in a Highly Antiaromatic Polycycle

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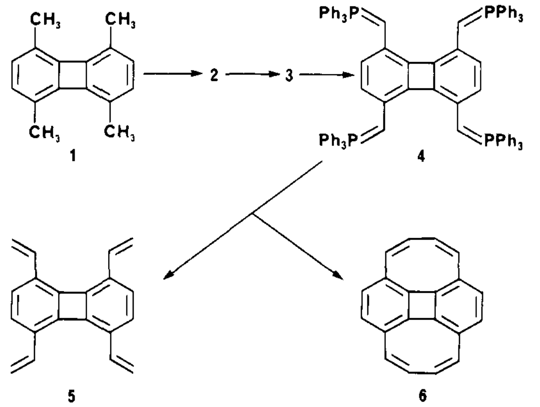
Part of the recent revival of interest in antiaromaticity and the associated magnetic phenomenon of ring current paratropism[1] has centered on the behavior of fused systems containing both $[4n]$- and $[4n + 2]\pi$ ring components.[1a,2] The known systems of this type have shown a mutual reduction of aromaticity/antiaromaticity in the component rings, as judged by changes in the chemical shifts of attached protons. We wish to report the synthesis of an unusual polycyclic hydrocarbon in which the $[4n]\pi$ component rings retain strongly antiaromatic ring current behavior, while the diatropic ring current effects in the neighboring benzene rings are completely quenched, resulting in *benzene rings having virtually no ring current.*

1,4,5,8-Tetramethylbiphenylene (**1**), prepared by the method of Friedman and Logullo,[3,4] was treated with 4 equiv of NBS in CCl_4 to give the benzylic tetrabromide **2** in 69% yield (Scheme I). Reaction of bromide **2** with excess PPh_3 (DMF, 100 °C) produced the corresponding tetrakis(phosphonium) salt **3** in 79% yield. Subsequent treatment of Me_2SO solutions containing **3** with either dimsyl potassium or KO-*t*-Bu (4 equiv) gave the tetrakis(ylide) **4** as a jet-black solution with suspended black crystalline solid. Ylide **4**, upon quenching with gaseous formaldehyde, gave a 69% yield of the bright yellow 1,4,5,8-tetravinylbiphenylene (**5**) after chromatography (silica, CCl_4): ^1H NMR ($CDCl_3$) δ 6.96 (4 H, s), 5.66 (4 H, dd, J_1 = 0.87, J_2 = 17.56 Hz), 5.34 (4 H, dd, J_1 = 0.87, J_2 = 10.96 Hz), 6.76 (4 H, dd, J_1 = 17.56, J_2 = 10.96 Hz).[5]

Scheme I



In a "double bis-Wittig" reaction,[6] dropwise addition of freshly prepared monomeric glyoxal[7] in THF to the ylide **4** produced a complex mixture of products, consisting primarily of a deep red insoluble polymer. Extractive workup followed by chromatography (silica, CS_2) gave the polycyclic hydrocarbon **6** in 1% yield, based upon **3**.

Dicyclooctabiphenylene **6** was isolated and stored as a deep blue solution in CS_2 with dilute solutions (0.2 mM) being stable for 1–2 weeks at −30 °C. Concentration of these solutions led to accelerated decomposition, which became virtually instantaneous at dryness. The compound could, however, be observed momentarily as a dark blue-black crystalline solid and could be transferred to other solvents by rapid redissolution.[8] Exclusion of light and/or oxygen had no effect on the rate of decomposition. No dimers could be identified in the insoluble yellowish decomposition products, which appeared to be polymeric in nature. Hydrocarbon **6** reacts readily with bromine in CS_2, decolorizing instantly to give a complex mixture of cycloocta-ring addition products.

The UV-visible spectrum of **6** shows highly structured absorptions which extend well into the visible region, tailing to over 750 nm.[9] Most intriguing, however, is the proton NMR spectrum of the hydrocarbon, which consists of a 4-H singlet at δ 4.55 and an 8-H multiplet at δ 3.61 ($CDCl_3$, 300 MHz). These values change only slightly (upfield) in other solvents. Computer-assisted spectral analysis of the 8-H AA′BB′ multiplet using LAOCOON III[10] gave chemical-shift values of 3.63 and 3.59 for the cycloocta ring protons of **6**, with coupling constants J_{AB} = 13.83, $J_{BB'}$ = 10.07, $J_{AB'}$ = −0.58, and $J_{AA'}$ = 1.25 Hz. The exact assignment of the cycloocta protons is not evident from either spectra or calculations (vide infra).

The extremely paratropic nature of **6** is made evident by comparing proton chemical shifts with the vinyl compound **5**. The

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(1) For example, see: (a) Scott, L. T.; Kirms, M. A.; Günther, H.; Puttkamer, H. v. *J. Am. Chem. Soc.* **1983**, *105*, 1372–1373. (b) Minsky, A.; Meyer, A. Y.; Poupko, R.; Rabinovitz, M. *Ibid.* **1983**, *105*, 2164–2172. (c) Carpenter, B. K. *Ibid.* **1983**, *105*, 1700–1701.

(2) (a) Wilcox, C. F., Jr.; Grantham, G. D. *Tetrahedron* **1975**, *31*, 2889–2895. (b) Obendorf, S. K.; Wilcox, C. F., Jr.; Grantham, G. D.; Hughes, R. E. *Tetrahedron* **1976**, *32*, 1327–1330. (c) Nakagawa, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 202–214. (d) Staab, H. A.; Gunthert, P. *Chem. Ber.* **1977**, *110*, 619–630. (e) Darby, N.; Cresp, T. M.; Sondheimer, F. *J. Org. Chem.* **1977**, 42, 1960. (f) Cresp, T. M.; Sondheimer, F. *J. Am. Chem. Soc.* **1977**, *99*, 194. (g) Günther, H.; Günther, M. E.; Mondeshka, D.; Schmickler, H.; Sondheimer, F.; Darby, N.; Cresp, T. M. *Chem. Ber.* **1979**, *112*, 71–83. (h) Hess, B. A., Jr.; Schaad, L. J.; Agranat, I. *J. Am. Chem. Soc.* **1978**, *100*, 5268–5271.

(3) Logullo, F. M.; Seitz, A. M.; Friedman, L. *Org. Synth.* **1968**, *48*, 12.

(4) All new compounds exhibited satisfactory spectral properties (NMR and/or UV). Those compounds capable of volatilization (**1**, **2**, and **5**) gave satisfactory analyses by high-resolution mass spectroscopy.

(5) Coupling constants for **5** result from an analysis using the NMR spectral program LAOCOON III (see ref 10).

(6) Vollhardt, K. P. C. *Synthesis* **1975**, 765–780.

(7) Harries, C.; Temme, P. *Chem. Ber.* **1907**, *40*, 165–172.

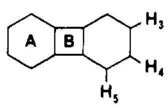
(8) The nonalternant hydrocarbon pyracylene behaves similarly: (a) Trost, B. M.; Bright, G. M. *J. Am. Chem. Soc.* **1967**, *89*, 4244; (b) *Ibid.* **1969**, *91*, 3689. (c) Trost, B. M.; Bright, G. M.; Frihart, C.; Brittelli, D. *Ibid.* **1971**, *93*, 737.

(9) (a) The electronic spectrum of **6** has been predicted: Vogler, H.; Ege, G. *J. Am. Chem. Soc.* **1977**, *99*, 4599–4604. (b) UV-vis for **6** (cyclohexane) (log ϵ): 208 (5.16), 249 (4.29), 260 (4.27), 271 (4.42), 282 (4.47), 294 sh (3.94), 309 (3.94), 322 (3.84), 338 sh (3.55), 358 (3.23), 386 sh (2.86), 425 (2.80), 456 (2.82), 484 (2.74), 557 (2.74), 596 (2.77), 648 sh (2.64), 702 sh (2.17) nm. (c) Further analysis of this data will be presented in a full paper.

(10) (a) Bothner-By, A. A.; Castellano, S. M. In "Computer Programs for Chemistry"; DeTar, D. F., Ed.; W. A. Benjamin: New York, 1968; Vol. 1. (b) Bothner-By, A. A.; Castellano, S.; *QCPE* **1967**, *10*, 111.

0002-7863/83/1505-7191$01.50/0

Table I. Ring Currents[a] and ^{1}H NMR Chemical Shifts[b] for Hydrocarbons 7, 8, and 6



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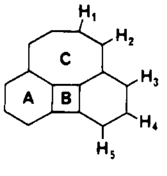

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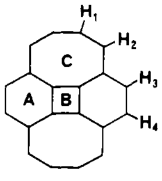

6

	compd		
	7	8	6
	Calculated Ring Current		
ring			
A	+0.608	+0.369	−0.091
B	−0.804	−0.745	−1.164
C		−0.706	−1.071
proton	Observed Chemical Shift		
1		4.61	3.63[c]
2		4.74	3.59[c]
3	6.73	5.83	4.55
4	6.73	6.21	4.55
5	6.62	6.05	

[a] Benzene = +1.00. This work; see ref 13a. [b] In ppm downfield from Me_4Si. 300-MHz spectra taken in $CDCl_3$, Me_4Si internal reference. Multiplets analyzed by LAOCOON III (ref 10). [c] Assignments given here assume a slightly paratropic ring current for A ring of 6. For an explanation of possible ambiguity, see ref 13b,c,d.

benzenoid protons in **6** show an upfield shift of 2.41 ppm relative to **5**, while the α and β cycloocta protons are shifted upfield by 3.15 and 1.73 ppm, respectively. The observed magnetotropism for this and similar compounds[11] appears to be well described by an iterative Hückel–McWeeny ring current model[12–14] (see Table I).

It is worthwhile to consider the qualitative origin of benzenoid atropism in **6**. In addition to three rings of $[4n]$ type, compound **6** has a coronoid topology with a central ring of $[4]\pi$ and a periphery of $[16]\pi$. While the importance of peripheral circuits has been shown for some systems,[8,15] the perturbation by the central substructure may be so great as to remove any simple predictive capability based solely upon the periphery.[16] Such peripheral analyses are, to some degree, implicit in the consideration of all conjugated circuits, as in the approaches of Randić[17] and Gomes.[18] According to these methods, benzenoid atropism in **6** arises from the net cancellation of numerous Hückel and anti-Hückel conjugated circuits, as opposed to the situation encountered in the Clar–Robinson "nonsextet" rings of polycyclic aromatics,[19] wherein reduced diatropism results from the virtual or complete absence of conjugated circuits involving the affected ring.[17b]

Registry No. 1, 63548-78-7; **2**, 87729-44-0; **3**, 87739-06-8; **4**, 87729-45-1; **5**, 87729-46-2; **6**, 64074-44-8; **7**, 259-79-0; **8**, 36230-20-3.

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(11) (a) Wilcox, C. F., Jr.; Uetrecht, J. P.; Grohman, K. K. *J. Am. Chem. Soc.* **1972**, *94*, 2532. (b) Wilcox, C. F., Jr.; Uetrecht, J. P.; Grantham, G. D.; Grohmann, K. G. *Ibid.* **1975**, *97*, 1914–1920.

(12) McWeeny, R. *Mol. Phys.* **1958**, *1*, 311.

(13) (a) Ring currents were calculated by a self-consistent HMO technique used previously (ref 11b). For an excellent discussion of ring currents in paratropic systems, see the following references. (b) Coulson, C. A.; Mallion, R. B. *J. Am. Chem. Soc.* **1976**, *98*, 592–598. (c) Gomes, J. A. N. F.; Mallion, R. B. *J. Org. Chem.* **1981**, *46*, 719–727. (d) Mallion, R. B. *Pure Appl. Chem.* **1980**, *52*, 1541–1548.

(14) Several more highly fused derivatives of **6** and **8** have now been prepared, and the observed proton chemical shifts correlated with ring current calculations. Complete synthetic, spectroscopic, and theoretical details will be presented in a full paper.

(15) (a) Platt, J. R. *J. Chem. Phys.* **1954**, *22*, 1448–1458. (b) Müllen, K. *Helv. Chim. Acta* **1978**, *61*, 2307. (c) Minsky, A.; Meyer, A. Y.; Hafner, K.; Rabinovitz, M. *J. Am. Chem. Soc.* **1983**, *105*, 3975–3981.

(16) This point is particularly evident in the case of cycloocta[*def*]biphenylene **8**.

(17) (a) Randić, M. *J. Am. Chem. Soc.* **1977**, *99*, 444–450; (b) *Pure Appl. Chem.* **1980**, *52*, 1587–1596.

(18) Gomes, J. A. N. F. *Theor. Chim. Acta* **1981**, *59*, 333–356.

(19) (a) Clar, E. "The Aromatic Sextet"; Wiley: London and New York, 1972. (b) Clar, E. "Polycyclic Hydrocarbons"; Academic Press: London and New York; Springer-Verlag: Berlin, 1964; Vol. 1.

A β-Metal Ketone Strategy. Reactions of Siloxycyclopropanes with Silver(I) Tetrafluoroborate and Copper(II) Tetrafluoroborate Leading to 1,6-Diketones

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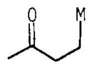
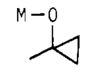
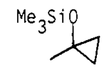
Development of new synthetic methodology for bond connection β to carbonyls constitutes one of the main challenging themes in modern organic synthesis.[1] For this purpose the use of β-metal-substituted ketones **1** would be most straightforward. However, the reported result of the reaction of **1** where the metal M is an alkali metal seems discouraging because of the inevitable isomerization of **1** to more stable form **2** by internal nucleophilic addition.[2,3] For the efficient carbon–carbon bond formation β to carbonyls the use of other elements such as transition metals for M in **1** seems attractive, although in general they are hardly accessible.[4,5]



1



2



3

Our strategy for **1** is that electrophilic ring opening of siloxycyclopropane **3** by naked (or ligand free) transition-metal ions will give β-transition-metal ketone **1** efficiently with elimination of a trialkylsilyl moiety.[6] Thus, the reactions of siloxycyclopropane **3** with silver(I) tetrafluoroborate, $AgBF_4$, and copper(II) tetrafluoroborate, $Cu(BF_4)_2$, have been studied. We wish to report here the new carbon–carbon bond-forming reaction in which the intervension of β-silver- or β-copper-substituted ketone as intermediates is suggested.

1-(Trimethylsiloxy)bicyclo[4.1.0]heptane(**4**) (5 mmol)[7] was added to the suspension of silver tetrafluoroborate ($AgBF_4$, 6 mmol) in anhydrous ether at -20 °C, under atmosphere of nitrogen. Over a period of 15 min the temperature was raised to 15 °C, while a silver mirror gradually appeared on the wall of the reaction vessel. After another 15 min, workup (aqueous NH_4Cl and aqueous $NaHCO_3$) and purification upon column

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(1) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239.

(2) Hamon, D. P. G.; Sinclair, R. W. *J. Chem. Soc., Chem. Commun.* **1968**, 890.

(3) A review for synthetic equivalent of β-lithio ketones; see: Werstiuk, N. H. *Tetrahedron* **1983**, *35*, 205.

(4) Stable β-transition-metal ketones **1**; see for (a) M = Hg: DePuy, C. H.; Lanen, J. U. *J. Org. Chem.* **1974**, *39*, 3360. (b) M = Pt: Green, M.; Howard, J. A. K.; Mitrprachachon, P,; Pffefer, M.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc. Dalton Trans.* **1979**, 306. (c) M = Co: Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 5284. (d) M = Mn: Bennet, W. A.; Robertson, G. B.; Watt, R.; Whimp, P. O. *J. Chm. Soc., Chem. Commun.* **1971**, 752. (e) M = Fe: Jensen, J. E.; Campbell, L. L.; Nakanishi, S.; Flood, T. C. *J. Organomet. Chem.* **1983**, *244*, 61.

(5) Recently, Kuwajima and Nakamura have reported the aldol condensation via and isolation of β-titano esters; see: Nakamura, E; Kuwajima, I. *J. Am. Chem. Soc.* **1983**, *105*, 651; **1977**, *99*, 7360.

(6) Synthesis of β-mercuri ketones from siloxycyclopropanes and some transformations from them via transmetalation; see: Ryu, I.; Matsumoto, K.; Ando, M.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1980**, *21*, 4283.

(7) (a) Murai, S.; Aya, T.; Sonoda, N. *J. Org. Chem.* **1973**, *38*, 4354. (b) Ryu, I.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1977**, 4611. (c) Girard, C.; Conia, J. M. *J. Chem. Res. Synop.* **1978**, 182.

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