The inherent sensitivity and simplicity make the new experiment generally applicable to a number of biological and chemical systems where observation of ^{15}N chemical shifts has proven time consuming or impossible because of the low natural abundance and NMR sensitivity of ^{15}N. Pulse sequences with more than one pulse applied to the observed nuclei[5] make suppression of unwanted signals harder and do, in practice, not provide the improvement that might be expected.[16]

Acknowledgment. The sample of gramacidin S was kindly provided by Professor D. H. Live (Rockefeller University). We are indebted to professor Gary Maciel for many valuable comments in preparing the manuscript and further gratefully acknowledge use of the Colorado State University Regional NMR Center, supported by National Science Foundation Grant CHE-8208821. A.B. acknowledges support from the Department of Energy (Laramie Energy Technology Center), and R.H.G. was supported by NSF Grant PCM 79-16861, awarded to C. D. Poulter.

Registry No. Gramicidin S, 113-73-5.

Activation of Methane by Iridium Complexes

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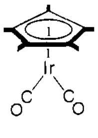
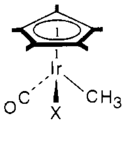
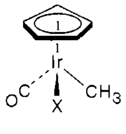
Methane occupies a unique place among the saturated hydrocarbons because of its abundance and availability and because of the strength of its carbon–hydrogen bonds.[1] As we recently reported,[4] irradiation of solutions of the (pentamethylcyclopentadienyl)iridium complex **1** in neopentane, cyclohexane, or benzene formed alkyl- or aryliridium hydrides, (η-C_5Me_5)Ir(CO)(H)R. We now describe the activation of methane by **1** and by a closely related iridium compound. Oxidative addition of methane to an organometallic complex to form a characterized product has not previously been reported.



1



2a X=H
2b X=Cl



3a X=H
3b X=Br

A solution of **1** in perfluorohexane under methane pressure of ca. 8 atm was irradiated for 16 h at room temperature.[5] After release of CH_4 pressure, the presence of (η-C_5Me_5)Ir(CO)(H)CH_3 (**2a**) in the C_6F_{14} solution was shown by new ^1H NMR signals at δ 1.99 (s, 15 H), 0.54 (s, 3 H), and -16.10 (s, 1 H) and IR bands at 2136 (vw, ν_{IrH}) and 1997 cm^{-1} (s, $\nu_{C\equiv O}$).[6] The yield of **2a** estimated from the NMR of the solution after irradiation was 20–25%.[8] By reaction with CCl_4, **2a** was converted to the very stable chloride derivative (η-C_5Me_5)Ir(CO)(Cl)CH_3 (**2b**).[9]

It was not convenient to use methane as the solvent in this reaction because of its low boiling point. Other potential solvents containing carbon–hydrogen bonds are likely to be reactive toward **1**. Use of perfluoroalkyl solvents circumvents this difficulty and broadens the range of photochemical reactions of **1** that can be conveniently studied.

The range of ligand properties compatible with aliphatic C–H activation is at this time far from clear. In all three systems that have been explicitly shown to activate C–H bonds in intermolecular fashion,[4,10,11] the pentamethylcyclopentadienyl group is involved as a ligand. We now report that in at least one case, the ordinary cyclopentadienyl group serves as well as its pentamethyl analogue.

A solution of (η-C_5H_5)Ir$(CO)_2$[12] (30 mg) in perfluorohexane (20 mL) under methane (ca. 10 atm) was irradiated for 6 h. As before, some material insoluble in C_6F_{14} formed during the irradiation, but from IR and NMR the only new compound in solution was (η-C_5H_5)Ir(CO)(H)CH_3 (**3a**).[13] From NMR intensities, the yield was ca. 20%, and the molar ratio of **3a** to remaining (η-C_5H_5)Ir$(CO)_2$ at this stage was 0.29. In a slow reaction with *N*-bromosuccinimide, **3a** was converted to the bromo derivative **3b**, which was fully characterized.[14]

In the intermediates we *presume* are involved in these reactions, the electron-rich character of the metal is expected to decrease in the order (η-C_5Me_5)Ir(PMe_3) > (η-C_5Me_5)Ir(CO) > (η-C_5H_5)Ir(CO). Even for the last member of the series, activation is facile,[15] and it remains to be seen how far the ligands can be altered before activation is forestalled.[16]

Several earlier studies have reported that metal atoms in methane matrices at 12–15 K form hydridomethyl species with[19a-c] or without[19d] irradiation. Very recently, Watson[20] reported the

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(1) Commonly quoted[2] bond-dissociation energies suggest that the C–H bond of methane is the strongest of all the alkanes and cycloalkanes. According to recent determinations,[3a] cyclopropane is an exception with *D*(H–cyclopropyl) = 106.3 ± 0.3 Kcal/mol;[3b] compare *D*(H–CH_3) = 105.1 ± 0.15 kcal/mol.[3c]

(2) For example: March, J. "Advanced Organic Chemistry"; 2nd ed.; McGraw-Hill: New York, 1977; p 175.

(3) (a) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493–532. (b) Baghal-Vayjooee, M. H.; Benson, S. W. *J. Am. Chem. Soc.* **1979**, *101*, 2838–2840. (c) Baghal-Vayjooee, M. H.; Colussi, A. J.; Benson, S. W. *Ibid.* **1978**, *100*, 3214–3215.

(4) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723–3725.

(5) In this experiment 50 mg **1** (more than would dissolve) in 20 mL of degassed perfluorohexane in a 75-mL quartz tube was placed 5 cm from a Hanovia 450-W medium-pressure mercury lamp fitted with a cylindrical Pyrex filter and a concentric water-cooled quartz jacket. The ^1H NMR spectrum of a saturated C_6F_{14} solution of **1** (ca. 0.0025 M) under 700 mm of CH_4 pressure showed singlets at δ 2.15 and 0.16 due to **1** and CH_4, respectively; the intensities indicated the molar ratio CH_4:**1** was ca. 14. Henry's law suggests that CH_4:**1** will be about 120 in the experiment described.

(6) We observe identical spectroscopic parameters for pure and fairly stable dilute C_6F_{14} solutions of **2a** (in the 0.01 M range) prepared by zinc reduction[7] of **2b**. Like its other alkyl analogues,[4] **2a** is unstable at room temperature as a concentrated solution or neat oil.

(7) Moss, J. R.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 75–79.

(8) The molar ratio **1**:**2a** in the solution at this stage was 3.0. No other new IR or NMR bands were observed, although some unidentified precipitate forms during irradiation.

(9) The yield of **2b**, purified by chromatography on Florisil, was 10 mg (19%). Since the **2a** to **2b** conversion is expected to be very efficient, the yield of **2b** is consistent with the spectroscopically estimated yield of **2a**. Properties of **2b**: yellow solid, mp 138–139 °C; IR (*n*-hexane) 2017 cm^{-1} ($\nu_{C\equiv O}$); ^1H NMR (CD_2Cl_2) δ 1.88 (s, 15 H), 1.05 (s, 3 H); MS (16 eV, 130 °C) M^+, $(M - CH_3)^+$, $(M - CH_3 - CO)^+$. Anal. ($C_{12}H_{18}ClIrO$) C, H.

(10) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352–354; **1983**, *105*, 3929–3939.

(11) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 686–687.

(12) Fischer, E. O.; Brenner, K. S. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1962**, *17B*, 774–775. For (η-C_5H_5)Ir$(CO)_2$: IR (C_6F_{14}) 2048, 1982 cm^{-1}; IR (*n*-hexane) 2041, 1974 cm^{-1}; ^1H NMR (C_6F_{14}) δ 5.36 (s); ^1H NMR (CD_2Cl_2) 5.55 (s).

(13) Properties of **3a**: IR (C_6F_{14}) 2174 cm^{-1} (vw, ν_{IrH}), 2017 cm^{-1} (s, $\nu_{C\equiv O}$); ^1H NMR (C_6F_{14}) δ 5.29 (s, 5 H), 0.99 (s, 3 H), −16.16 (s, 1 H). At room temperature, the compound is stable in dilute solution and does not react with CCl_4.

(14) Properties of **3b**: yellow solid, mp 114–116 °C; IR (*n*-hexane) 2039 cm^{-1} ($\nu_{C\equiv O}$); ^1H NMR (CD_2Cl_2) δ 5.66 (s, 5 H), 1.70 (s, 3 H); MS (16 eV, 150 °C) M^+, $(M - CH_3)^+$, $(M - CO)^+$, $(M - CH_3 - CO)^+$. Anal. (C_7H_8BrIrO) C, H.

(15) Neopentane also adds oxidatively to (η-C_5H_5)Ir$(CO)_2$, and the reactions appear general.

(16) Many examples of intermolecular *aromatic* C–H activation are known,[17] and it was shown some years ago that under irradiation (η-C_5H_5)Ir$(CO)_2$ oxidatively added benzene.[18]

(17) (a) Parshall, G. W. *Catalysis* (*London*) **1977**, *1*, 335–367. (b) Muetterties, E. L. *Chem. Soc. Rev.* **1982**, *11*, 283–320.

(18) Rausch, M. D.; Gastinger, R. G.; Gardner, S. A.; Brown, R. K.; Wood, J. S. *J. Am. Chem. Soc.* **1977**, *99*, 7870–7876.

(19) (a) Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave J. L. *J. Am. Chem. Soc.* **1980**, *102*, 7394–7396. (b) Ozin, G. A.; McIntosh, D. F.; Mitchell, S. A. *Ibid.* **1981**, *103*, 1574–1575. (c) Ozin, G. A.; McCaffrey, J. G. *Ibid.* **1982**, *104*, 7351–7352. (d) Klabunde, K. J.; Tanaka, Y. *Ibid.* **1983**, *105*, 3544–3546.

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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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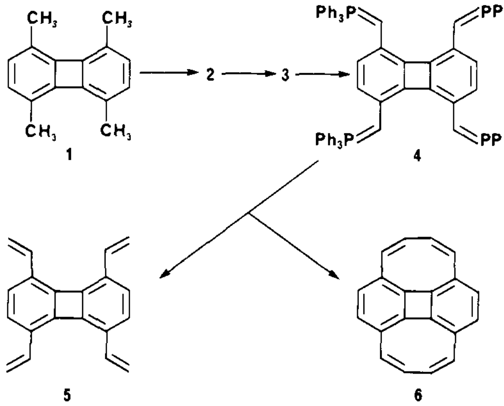
Part of the recent revival of interest in antiaromaticity and the associated magnetic phenomenon of ring current paratropism[1] has centered on the behavior of fused systems containing both [4*n*]- and [4*n* + 2]π ring components.[1a,2] The known systems of this type have shown a mutual reduction of 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 [4*n*]π 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.

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