Silver Complexation by σ C−H Bonds: Interaction of Silver with *meso*-Octaethyltetraoxaporphyrinogen

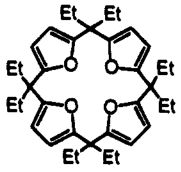
Christine M. Kretz,† Emma Gallo,† Euro Solari,†
Carlo Floriani,*,† Angiola Chiesi-Villa,‡ and Corrado Rizzoli‡

Institut de Chimie Minérale et Analytique
BCH, Université de Lausanne
CH-1015 Lausanne, Switzerland
Dipartimento di Chimica
Università di Parma
I-43100 Parma, Italy

Received May 13, 1994

The complexation of C−H σ bonds by metals is a key step in the metal-assisted activation of hydrocarbons.[1,2] In contrast to the isolation of numerous dihydrogen complexes,[3] the steric hindrance and the weak basicity of the C−H bond *vs* the H−H bond have thus far precluded the isolation of hydrocarbon σ-bonded complexes.[4] The C−H−M interaction has been structurally or spectroscopically detectable only when C−H is part of a previously bound ligand,[4,5] taking advantage of chelate or proximity effects.

The intermolecular (C−H)−M interactions we report here originate from strategies adopted to provoke a σ C−H bond complexation. The strategy employs the very carbophilic silver(I) cation and a binding cage with a preorganized set of sterically unhindered C−H bonds. The interaction of silver(I) triflate has been explored with the *meso*-octaethyltetraoxaporphyrinogen, Et_8O_4 (**1**).



Et_8O_4, 1

The *meso*-octaalkyltetraoxaporphyrinogen derivatives, a class of previously synthesized macrocyclic compounds,[6] have showed no reactivity toward metals.[6c,e,f,h] The structure of **1**[7] shows, however, a double saddle-shaped conformation with two cavities where both the C=C and methine C−H bonds are exposed and accessible to appropriate metal cations. The reaction of **1**[8] with silver triflate produces dimer **2**.[9]

$$\underset{\mathbf{1}}{2Et_8O_4} + 2AgSO_3CF_3 \rightarrow \underset{\mathbf{2}}{[Et_8O_4AgSO_3CF_3]_2}$$

The structure of the centrosymmetric dimer **2** is shown in Figure 1.[10] The conformation and other structural parameters of the macrocycle[11] are only very slightly affected by coordination. The structure of **2** shows two major interesting features. Most notable is a significant example of a (C−H)−M triangular arrangement, characteristic of a 3c-2e interaction. Two axial coordination sites are filled by two C−H bonds around a pseudooctahedral silver cation. The most relevant structural parameters defining this interaction are (i) the distances, Ag−C2, 2.499(12) Å; Ag−H2, 2.43 Å; Ag−C13, 2.465(12) Å; Ag−H13, 2.62 Å; (ii) the angles, C2−H2−Ag, 85°; C13−H13−Ag, 70°; Ag−C2−H2, 75°; Ag−C13−H13, 91°; C1*−Ag−C2*, 172°; and (iii) the dihedral angles between the O1,C1,C2,C3,C4 mean plane and Ag−C1* and between the

---

(1) (a) Davies, J. A.; Watson, P. L.; Liebman, J. F.; Greenberg, A. *Selective Hydrocarbon Activation*; VCH: New York, 1990. (b) *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; Wiley: New York, 1989. (c) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Reidel: Ingham, MA, 1984. (d) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *2*, 91. (e) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403. (f) Sen, A. *Acc. Chem. Res.* **1988**, *21*, 421. (g) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

(2) (a) Rothwell, I. P. The Homogeneous Activation of Carbon−Hydrogen Bonds by Electrophilic Metal Systems; Selective Hydrocarbon Activation; VCH: New York, 1990; Chapter 3. (b) Watson, P. L. C−H Bond Activation with Complexes of Lanthanides and Actinide Elements. Selective Hydrocarbon Activation; VCH: New York, 1990; Chapter 4. (c) Rothwell, I. P. The Homogeneous Activation of Carbon−Hydrogen Bonds by High Valent Early d-Block, Lanthanides and Actinide Metal Systems. In *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; Wiley: New York, 1989; Chapter 5.

(3) (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (c) Jessop, P. J.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (d) *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: Weinheim, Germany, 1992. (e) Heinekey, D. W.; Oldham, M. J. *Chem. Rev.* **1993**, *93*, 913.

(4) (a) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299. (b) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789 and references therein.

(5) (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(6) (a) Ackman, R. G.; Brown, W. H.; Wright, G. F. *J. Org. Chem.* **1955**, *20*, 1147. (b) Brown, W. H.; French, W. N. *Can. J. Chem.* **1958**, *36*, 371. (c) Chastrette, M.; Chastrette, F. *J. Chem. Soc., Chem. Commun.* **1973**, 534. (d) Kobuke, Y.; Hanji, K.; Horiguchi, K.; Asada, M.; Nakayama, Y.; Furukawa, J. *J. Am. Chem. Soc.* **1976**, *98*, 7414. (e) Rest, A. J.; Smith, S. A.; Tyler, I. D. *Inorg. Chim. Acta* **1976**, *16*, L1. (f) Corsini, A.; Panoyan, J. M. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1449. (g) Newkome, G. R.; Sauer, J. D.; Roper, J. M.; Hager, D. C. *Chem. Rev.* **1977**, *77*, 513. (h) de Sousa Healy, M.; Rest, A. J. *J. Chem. Soc., Perkin Trans. I* **1985**, 973. (i) Vogel, E.; Haas, W.; Knipp, B.; Lex, J.; Schmickler, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 406. (j) Musau, R. M.; Whiting, A. *J. Chem. Soc., Chem. Commun.* **1993**, 1029.

(7) The X-ray analysis on **1** will not be reported in detail, even though the most significant structural parameters are used in the discussion of the structure of **2**.

(8) Procedure for **1**: the synthesis of **1** has been performed using a slight modification of the procedures reported in refs 6a−c. ^1H NMR (CD_2Cl_2): δ 5.97 (s, CH, 8H), 1.83 (q, $J = 7$ Hz, CH_2, 16H), 0.56 (t, $J = 7$ Hz, CH_3, 24H). ^{13}C NMR (CD_2Cl_2, 284 and 230 K): δ 156.50 (s, O*C*CH), 105.17 (d, $J = 173$ Hz, CH), 43.88 (s, *C*Et$_2$), 24.54 (t, $J = 129$ Hz, *C*H$_2$), 7.22 (q, $J = 127$ Hz, *C*H$_3$). Anal. Calcd for $C_{36}H_{48}O_4$: C, 79.37; H, 8.88. Found: C, 79.28; H, 8.61.

(9) Procedure for **2**: a mixture of **1** (2.50 g, 4.60 mmol) and AgO_3SCF_3 (1.18 g, 4.60 mmol) was dried under vacuum, and CH_2Cl_2 (125 mL) was added. The light suspension was allowed to stir for 15 h at room temperature. The solution was then filtered and concentrated to dryness. Complex **2** was recrystallized from a mixture of CH_2Cl_2/hexane (1:10) and then washed with hexane to give a pale pink microcrystalline solid which was dried *in vacuo* (75%). ^1H NMR (CD_2Cl_2): δ 6.27 (br, CH, 8H), 1.92 (br, CH_2, 16H), 0.61 (t, CH_3, 24H). ^{13}C NMR (CD_2Cl_2, 290 K): δ 158.87 (s, O*C*CH), 103.44 (d, $J = 180$ Hz, *C*H), 45.41 (s, *C*Et$_2$), 24.36 (t, $J = 129$ Hz, *C*H$_2$), 7.35 (q, $J = 125$ Hz, *C*H$_3$). ^{13}C NMR (CD_2Cl_2, 233 K): δ 163.15, 155.35 (2s, O*C*CH and O*C′*CH), 106.78 (d, $J = 168$ Hz, *C*H), 101.00 (d, $J = 179$ Hz, *C′*H), 45.77 (s, *C*Et$_2$), 25.12, 24.33 (2t, $J = 131$ Hz, *C*H$_2$ and *C′*H$_2$), 8.02 (q, $J = 125$ Hz, CH_3). For cases where two signals are observed for one type of carbon, the unprimed and primed C refer to those atoms closest to and furthest away from the silver atom, respectively. Anal. Calcd for $C_{37}H_{48}AgF_3O_7S$: C, 55.44; H, 5.99. Found: C, 55.96; H, 6.30.

(10) Crystal data for **2**: $C_{74}H_{96}Ag_2F_6O_{14}S_2 \cdot 4CH_2Cl_2$, $M = 1943.1$, triclinic, space group $P\bar{1}$, $a = 13.736(3)$ Å, $b = 14.595(3)$ Å, $c = 11.719(2)$ Å, $\alpha = 98.14(2)°$, $\beta = 100.82(2)°$, $\gamma = 73.18(2)°$, $V = 2199.4(8)$ Å^3, $Z = 1$, $\varrho_{calcd} = 1.467$ g cm^{-3}, $F(000) = 1000$, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 7.99 cm^{-1}; crystal dimensions 0.10 × 0.18 × 0.28 mm. The structure was solved by the heavy atom method and anisotropically refined for all non-hydrogen atoms. One dichloromethane solvent molecule of crystallization was found to be affected by disorder. The best fit was obtained by considering the Cl4 atom to be statistically distributed over two positions (A and B) anisotropically refined with site occupation factors of 0.6 and 0.4, respectively. The hydrogen atoms of the complex were located from a difference map and introduced as fixed contributors in the last stage of refinement ($U_{iso} = 0.08$ Å^2). The H atoms of the CH_2Cl_2 solvent molecules were ignored. For 3942 unique observed reflections [$I > 2\sigma(I)$] collected at $T = 123$ K ($5 < 2\theta < 50°$) and corrected for absorption, the final R was 0.063 (unit weights). All calculations were carried out with use of SHELX-76 on an Encore E91 computer. See supplementary material for more details.

(11) (a) The dihedral angles between the oxygen atoms plane and the furan rings are 80.4(1)°, 82.3(1)°, 83.6(1)°, 83.1(1)°, and 89.5(3)°, 81.5(3)°, 87.7(3)°, 78.2(3)° for $O4_A$, $O4_B$, $O4_C$, $O4_D$, in **1** and **2**, respectively, with A, B, C, and D referring to the furan rings containing O1, O2, O3, and O4, respectively. (b) The distances between the opposite carbon atoms are C2−C13, 5.49 Å, 4.93 Å; C3−C12, 5.47 Å, 5.00 Å; C8−C17, 5.46 Å, 5.61 Å; and C7−C18, 5.45 Å, 5.62 Å for **1** and **2**, respectively. (c) Bond distances and angles in the furan rings are not affected upon coordination, the average values being Cα−Cβ, 1.358(5)°, 1.354(8)° and Cβ−Cγ, 1.435(3)°, 1.442(13)° for **1** and **2**, respectively.

0002-7863/94/1516-10775$04.50/0

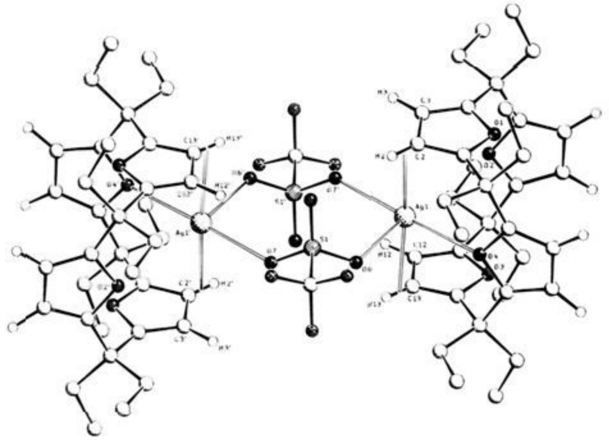


Figure 1. SCHAKAL view showing the dimer **2**. Selected bond distances (Å) and angles (deg): Ag1−C1*, 2.43; Ag1−C2*, 2.51; Ag1−O4, 2.743(6); Ag1−O6, 2.477(6); Ag1−O7′, 2.420(7); O6−Ag1−O7, 90.5(2); C2*−Ag1−O7′, 98.0; C2*−Ag1−O6, 84.4; C2*−Ag1−O4, 90.4; C1*−Ag1−O7′, 82.8; C1*−Ag1−O6, 87.9; C1*−Ag1−O4, 88.1; C1*−Ag1−C2*, 172.3; O4−Ag1−O6, 84.3(2); O4−Ag1−O7′, 169.7(2). Prime denotes a transformation of −*x*, 1 − *y*, 1 − *z*. C1* and C2* refer to the midpoints of the C2−H2 and C13−H13 bonds, respectively.

O3,C11,C12,C13,C14 mean plane and Ag−C2*, which are in both cases 86° (C1* and C2* refer to the midpoints of the C2−H2 and C13−H13 bonds).[12] The equatorial plane is determined by a set of four oxygen atoms, O6, O7′, O4, and O2, the first two being bound to silver at a normal distance, O4 at a further distance of 2.743 Å (accounting for a rather weak interaction), and O2 at a nonbonding distance of 3.906(9) Å.[13] By a rather small translation, parallel to the C3−C2 and C13−C12 bonds, the silver cation can be reset in an equivalent coordination position with the same set of equatorial oxygens, but with an exchange of O2 for O4 and the axial positions occupied by the C3−H3 and C12−H12 bonds. This hypothesis was supported by the solution behavior of **2** as compared to that of the free ligand **1**.

In the ^{1}H NMR spectrum of **1**, both at room temperature and at low temperature, a singlet for the methine protons was observed, while in **2** there are two resonances observed at 245 K. At room temperature, a fluxional process averages all of the furan rings, while at low temperature this process is slowed, and we observe the two resonances corresponding to two sets of furans in complex **2**. The splitting in the ^{1}H-coupled ^{13}C NMR spectrum of the single methine carbon doublet into two doublets upon cooling to 233 K is in agreement with the splitting observed in the low-temperature ^{1}H NMR spectrum. We also observed a small but significant difference (11 Hz) in the $J_{C,H}$ of these two doublets at low temperature for **2** but not for **1**. The smaller coupling constant may be associated with the interaction of the C−H bond of four methine carbon atoms bound to the silver cation, with the larger one corresponding to the four unbound methine carbon atoms.[4]

Electrophilic interactions of silver salts with olefins,[14] alkynes,[14] and arenes[15] have been mentioned, but a cagelike interaction with four C−H bonds has not been reported. Our system is unique in this type of interaction and in the fact that of all the possible types of coordination with **1** and with CH_2Cl_2,[16] this is the preferred bonding mode for silver triflate. Numerous examples of C−H agostic interactions have been described,[1a,3,5] but this type of side-on interaction of a C−H bond has never been explicity reported as the primary interaction.[1,2,4] The macrocycle **1** is currently under investigation as a possible unique cage for electrophilic metals prone to react with C−H and C=C functionalities.

Acknowledgment. We would like to thank the Fonds National Suisse de la Recherche Scientifique (Grant No. 20-33420-92) for financial support.

Supplementary Material Available: Experimental details associated with data collection, fractional atomic coordinates, fractional atomic coordinates for hydrogen atoms, thermal parameters, and bond distances and angles (7 pages); listing of observed and calculated structure factors for complex **2** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

[12] Some additional parameters concerning the atoms close to Ag, though we consider them as noninteracting, are Ag−C1, 2.948(10) Å; Ag−C3, 2.943(13) Å; Ag−C12, 2.956(10) Å; Ag−C14, 2.893(11) Å; Ag−C2−C1, 94.7(7)°; Ag−C2−C3, 103.8(9)°; Ag−C13−C12, 94.3(7)°; Ag−C13−C14, 94.3(7)°. This may be relevant to the known asymmetric interactions of Ag with C−C bonds in silver−arene complexes (see ref 15).

[13] For typical Ag−O bond distances, see: Shiro, M.; Koyama, H. *J. Chem. Soc. B* **1970**, 243. Barnes, J. C.; Paton, J. D. *Acta Crystallogr., Sect. B, Cryst. Struct. Commun.* **1984**, *40*, 72.

[14] van Koten, G.; Noltes, J. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1981; Vol. 2, Chapter 14.

[15] (a) Turner, R. W.; Amma, E. L. *J. Am. Chem. Soc.* **1966**, *88*, 3243. Hall Griffith, E. A.; Amma, E. L. *J. Am. Chem. Soc.* **1974**, *96*, 743. (b) Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 5955. (c) Kang, H. C.; Hanson, A. W.; Eaton, B.; Boekelheide, V. *J. Am. Chem. Soc.* **1985**, *107*, 1979. (d) Gano, J. E.; Subramaniam, G.; Birnbaum, R. *J. Org. Chem.* **1990**, *55*, 4760.

[16] Colsman, M. R.; Noirot, M. D.; Miller, M. M.; Anderson, O. P.; Strauss, S. N. *J. Am. Chem. Soc.* **1988**, *110*, 6886. Newbound, T. D.; Colsman, M. R.; Miller, M. M.; Wulfsberg, G. P.; Anderson, O. P.; Strauss, S. N. *J. Am. Chem. Soc.* **1989**, *111*, 3762. Colsman, M. R.; Newbound, T. D.; Marshall, L. J.; Noirot, M. D.; Miller, M. M.; Wulfsberg, G. P.; Frye, J. S.; Anderson, O. P.; Strauss, S. N. *J. Am. Chem. Soc.* **1990**, *112*, 2349 and references therein.