zation period and the beginning of the ^{13}C data acquisition. The magnetization of the protonated carbons decays more rapidly than that of the tertiary carbons by relaxation with the nearby protons and decays to zero during the delay time. In this way the signals from C-1–C-6 of the host molecules are invariable eliminated. However, substantial signals are obtained for all the resonances of the guest molecule, protonated or not; furthermore, signals are also obtained from pendant substituents of the host, such as the methoxyl and acetoxyl moieties. These signals reflect the various additional degrees of freedom available to all those carbon atoms.

We conclude from this study that ^{13}C CP/MAS provides an ideal analytical tool to study not only the primary composition of complexes of the cyclodextrins. Extensions to studies of thermal, photochemical, and biological stability should be of great utility in the design of industrially useful complexes. For example we have shown that benzene-d_6 "distills" from the annulus of the 2,6-di-*O*-Me-β-CD on heating above ambient temperatures; however, when the experiment is performed in a sealed tube a thermal equilibrium exists between the guest and host.

The data obtained from the deuterium quadrupole echo experiment appear to have immense potential in studies of many other species of "guest–host" complexation, including the binding of substrates and inhibitors to solid or immobilized enzymes. The recent report by Eckman and Vega[13] of zeolite complexation of *p*-xylene is an elegant illustration of this point. These and other studies of host–guest complexes in the solid state will be discussed further.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for operating grants (67-1905) and a referee for helpful comments, which we have been glad to include in this final manuscript.

---

[13] Eckman, R.; Vega, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 4841-4842.

Synthesis and Characterization of a Novel Bis(cyclopentadienyl)titanium Hydride Complex

Edmond Samuel

Laboratoire de Chimie Organique Industrielle, ENSCP
75005 Paris, France

John F. Harrod*

Chemistry Department, McGill University
Montreal, Canada H3A 2K6

Received November 17, 1983

We report below the synthesis and characterization of an unusual titanocene hydride complex. The complicated history of the "titanocenes" and their hydride derivatives has recently been reviewed by Toogood and Wallbridge.[1] Despite the variety of titanium hydride compounds reported, they are still a rather poorly characterized class of compounds in comparison to the hydrides of other transition metals. The only simple, terminal hydride of Ti(IV) known is the compound $(Cp^*)_2TiH_2$ ($Cp^* = \eta^5$-pentamethylcyclopentadienyl) reported by Bercaw et al.[2]

Reaction of certain organosilanes with $Cp_2Ti(CH_3)_2$ under ambient conditions, either in neat silane or in hydrocarbon solvents, leads to the remarkable and complicated reaction (1), where **2** = (e.g.) $PhSiH_3$, $(RO)_3SiH$, or $CH_3(RO)_2SiH$ but not halo-, trialkyl-, or triarylsilane.

$$\underset{\mathbf{1}}{4Cp_2Ti(CH_3)_2} + \underset{\mathbf{2}}{8R_3SiH} \rightarrow \underset{\mathbf{3}}{2[(Cp_2TiH)_2H]} + 6R_3SiCH_3 + R_6Si_2 + 2CH_4 \quad (1)$$

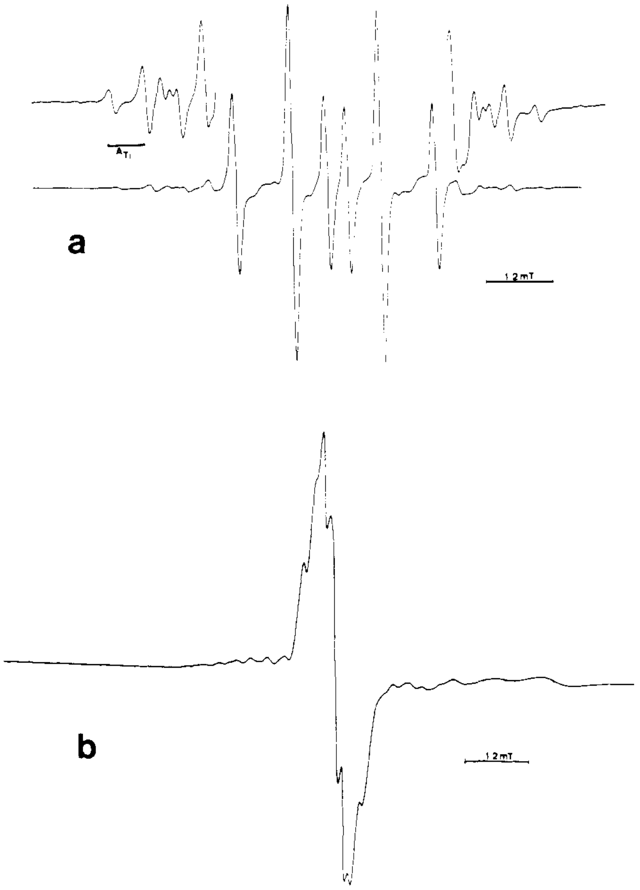


Figure 1. ESR spectra in toluene at room temperature (a) of **3** and (b) of the deuterated compound $(Cp_2TiD)_2D$.

Following admixture of the reactants in hexane under argon, the solution remains yellow for a period ranging from a few minutes to a few hours, depending on the reaction conditions. After the induction period, the onset of reaction is evident from the appearance of inky blue patches which propagate rapidly through the medium until the whole solution is intensely blue in color. The appearance of the blue color is accompanied by the evolution of a gas, which was shown by IR spectroscopy to be methane. Soon after the color change, blue-black crystals of the hydride **3** begin to deposit and after several hours, large, well-formed crystals may be recovered. In the case of $PhSiH_3$, the presence of the silicon-containing products in appropriate amounts was established by NMR spectroscopy.

The appearance of the dark blue color is also accompanied by an intense ESR signal (Figure 1a) which persists indefinitely in the absence of oxygen. This signal may also be observed in hydrocarbon solutions of freshly prepared **3**, following isolation, washing, and redissolving. These manipulations always result in some decomposition, as is evident from the appearance of a broad singlet slightly upfield of the signal due to **3**. Since the same blue compound results from the reactions of several different silanes, has an analysis corresponding closely to $C_{10}H_{10}Ti$,[3] and can also be made from dibenzyltitanocene (but not from the diphenyl analogue), the spectrum in Figure 1a is almost certainly due to the coupling of an unpaired electron on titanium to hydrogen atoms. This was confirmed by measuring the spectrum of the

---

[1] Toogood, G. E.; Wallbridge, M. G. H. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 267.

[2] Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219. Bercaw, J. E. *Ibid.* **1974**, *96*, 5087.

[3] Although analyses are excellent for the Cp_2Ti unit, the overall analyses have thus far not been satisfactory for the proposed formulation. Alkoxysilanes always give a small amount of contamination with alkoxytitanium(III) species, and other silanes give polysilane contaminants. Although the compound **3** is initially precipitated as well-formed crystals, we have not succeeded in recrystallizing it without decomposition. The crystal structure of **3** is presently under investigation.

0002-7863/84/1506-1859$01.50/0 © 1984 American Chemical Society

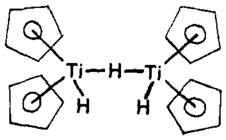
product of the reaction of **1** with $PhSiD_3$ to give a product with the expected reduction of the hyperfine interaction (a_H/a_D = 6.5141) as depicted in Figure 1b.

The features in Figure 1 exhibit a central multiplet (g = 1.9937) flanked by clearly resolved satellite splittings due to hyperfine interaction of the unpaired electron with Ti.[4] The central multiplet is composed of six lines, a doublet of triplets whose intensities correspond exactly to those expected for an unpaired electron interacting with two equivalent hydrogens ($a_{H(1)}$ = 0.97 mT) and a third hydrogen of different environment ($a_{H(2)}$ = 1.56 mT). The H(2) value is to our knowledge the highest value reported for Ti–H in a paramagnetic species. An important clue to the true nature of this compound is provided by a detailed analysis of the spectrum and by evaluation of the titanium hyperfine interaction constant (0.52 mT). The observed value is about one half of that normally observed for monomeric Ti(III) compounds and close to that expected for a single unpaired electron exchanging between two titanium centers.[5,6] The absence of features in the spectrum due to a triplet state (no $\Delta M_S = 2$ transition at midfield in the frozen glass solution spectrum) on the one hand and the pattern of the isotope spectrum at room temperature on the other exclude the possibility of a dimer containing two Ti(III) centers and leave a mixed oxidation state Ti(III)/Ti(IV) dimer as the most reasonable alternative. This is further corroborated by the observation of an intense absorption band [λ_{max} = 655 nm; ϵ (minimum value) = 1200 per electron] in the electronic spectrum of the compound in hexane. Such absorptions are characteristic of mixed-valence compounds and conform to class III behavior in the classification of Robin and Day.[7]

Infrared spectra in Nujol of freshly prepared **3** show, in addition to the usual cyclopentadienyl bands due to the titanocene structure, a strong band due to Ti–H at 2000 cm^{-1} (shifted to 2010 cm^{-1} in hexane). In the deuterated compound the terminal Ti–D stretch is observed at 1490 cm^{-1} [ν(Ti–H)/ν(Ti–D) = 1.36]. A broad band of moderate intensity at 1220–1250 cm^{-1}, absent in the deuterated compound, may be attributed to a Ti–H–Ti mode.[8]

Reaction of **3** with carbon tetrachloride leads to its rapid destruction and to the formation of both Cp_2TiCl_2 and chloroform. This confirms that the integrity of the Cp ring is conserved in **3** and further supports the presence of an active hydride.

Taken together, the evidence outlined above leaves little doubt that the structure of the compound **3** is that shown below. The



3

molecule is shown in a cis configuration for ease of representation, but it is more likely to adopt the trans configuration.

The detailed chemistry of **3**, particularly with respect to its interesting catalytic properties, will be reported elsewhere.[9]

Acknowledgment. J.F.H. thanks the French government for a sabbatical leave fellowship to aid in carrying out this project. We are grateful to Dr. D. Gourier for advice on the interpretation of ESR spectra and to J. Henique for efficient technical assistance.

Registry No. 1, 1271-66-5; **3**, 88825-84-7; **3**-d_3, 88825-85-8; $PhSiH_3$, 694-53-1; $PhSiD_3$, 18164-03-9.

---

(4) Ti isotopes of mass 47 and 49 have spins (abundances) of $^5/_2$ (7.75%) and $^7/_2$ (5.51%), respectively. Analysis of the hyperfine interactions with Ti isotopes in dimeric complexes has recently been discussed in detail by Francesconi et al.[5] By their interpretation, the central sextet in our spectrum is due to an unpaired electron interacting with two titaniums ($I = 0$, $I = 0$), 76.06%. The satellites observable on the wings at moderate gains are due to Ti($I = 0 + I = {}^5/_2$), 12.7%, and Ti($I = 0 + I = {}^7/_2$), 9.61%. At high gain, satellite bands due to Ti($I = {}^5/_2 + I = {}^5/_2$), 0.53%, Ti($I = {}^7/_2 + I = {}^5/_2$), 0.82%, and Ti($I = {}^7/_2 + I = {}^7/_2$), 0.30%, are observed. The hyperfine coupling constant is evaluated by measuring the separation between the clearly resolved satellites at low field.

(5) Francesconi, L. C.; Corbin, D. R.; Clauss, A. W.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1981**, *20*, 2059.

(6) Krusic, P.; Tebbe, F. N. *Inorg. Chem.* **1982**, *21*, 2900.

(7) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

(8) Bercaw, J. E.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1969**, *91*, 7301. Brintzinger, H. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 6182.

(9) The most important and novel catalysis effected by this and certain other titanium compounds is the polymerization of primary silanes to linear polysilanes. Details of this reaction will be published elsewhere.

Resonance Raman Study of Subunit Assembly Dependent Photoreduction of Heme of Extracellular Giant Hemoglobin

Teizo Kitagawa,* Sosuke Chihara, Kenzo Fushitani,[1] and Hideki Morimoto

Institute for Molecular Science
Okazaki National Research Institutes
Myodaiji, Okazaki, 444 Japan
Faculty of Engineering Science, Osaka University
Toyonaka, Osaka, 560 Japan

Received November 29, 1983

Extracellular giant hemoglobin (Hb) with $M_r = (3–4) \times 10^6$, found in various invertebrates[2a,b] and sometimes categorized as erythrocruorin, is composed of two superposed hexagonal disks made up of six subunits, ~110 Å in diameter.[3] The $^1/_{12}$ subunit assumes a molecular weight of $M_r = (2–3) \times 10^5$. The effect of salts upon the O_2 affinity is opposite between the giant Hb and tetrameric Hb's of blood red cells;[4] cations such as Mg^{2+} and Ca^{2+} increase the O_2 affinity of the giant Hb while they have no effect on human Hb, and anions such as Cl^- and DPG lower the O_2 affinity of the latter while they have no effect on the former. It seems important to elucidate how the distinct molecular properties of the giant Hb depend upon the subunit assembly.

Resonance Raman (RR) spectroscopy yields the heme vibrational spectrum, which is sensitive to the electronic structure as well as the stereostructure of heme.[5,6] The technique has in fact revealed the quaternary structure dependence of the strain exerted on the Fe–histidine (F8) bond by globin of deoxyHb[7,8] and also the quaternary structure dependent photoreduction of metHb by laser light.[9] Accordingly, the RR spectrum can be used to explore whether the heme structure of the giant Hb depends on subunit assembly. We report here an unexpected observation that the heme of the giant Hb undergoes wavelength-dependent photoreduction when the Hb is intact or dissociated into the $^1/_{12}$ subunit, but not when the Hb is dissociated into smaller assemblies.

An extracellular giant Hb containing protoporphyrin IX was isolated from an annelid, *Travisia japonica*. The preparation procedures of the intact Hb ($M_r = 3 \times 10^6$), the $^1/_{12}$ subunit ($M_r = 2.4 \times 10^5$), an assembly (M_r = 26 000), and separated chains (M_r = 14 000–18 000) are described elsewhere.[10a,b] The dissociation into the $^1/_{12}$ subunit was reversed by incubation in 0.2 M sodium phosphate buffer, pH 6.0, in the presence of the native

---

* Address correspondence to this author at the Institute for Molecular Science.

(1) Osaka University.

(2) (a) Chung, M. C. M.; Ellerton, D. *Prog. Biophys. Mol. Biol.* **1979**, *35*, 53–102. (b) Antonini, E.; Rossi-Fanelli, A.; Caputo, A. *Arch. Biochem. Biophys.* **1962**, *97*, 336–342.

(3) Kapp. O. H.; Vinogradov, S. N.; Ohtsuki, M.; Crewe, A. V. *Biochim. Biophys. Acta* **1982**, *704*, 546–548.

(4) Weber, R. E. *Nature* (*London*) **1981**, *292*, 386–388.

(5) Asher, S. *Methods Enzymol.* **1981**, *76*, 371–413.

(6) Rousseau, D. L.; Ondrias, M. R. *Annu. Rev. Biophys. Bioeng.* **1983**, *12*, 357–380.

(7) Nagai, K.; Kitagawa, T.; Morimoto, H. *J. Mol. Biol.* **1980**, *136*, 271–289.

(8) Ondrias, M. R.; Rousseau, D. L.; Shelnutt, J. A.; Simon, S. R. *Biochemistry*, **1982**, *21*, 3428–3437.

(9) Kitagawa, T.; Nagai, K. *Nature* (*London*) **1979**, *281*, 503–504.

(10) (a) Fushitani, K.; Ochi, O.; Morimoto, H. *Comp. Biochem. Physiol. B* **1982**, *72B*, 267–273. (b) Fushitani, K.; Ochi, O.; Morimoto, H. *Arch. Biochem. Biophys.* **1982**, *218*, 540–547.

0002-7863/84/1506-1860$01.50/0 © 1984 American Chemical Society