solutions of decamethyltitanocene are exposed to hydrogen gas, H_2 is absorbed to form a titanocene hydride complex which is stable at −80° even under vacuum. When warmed to room temperature under vacuum, however, the resulting species releases its coordinated hydrogen again.[8] The detailed structure of this hydride complex is presently under investigation.

Reversible reactions with hydrogen have been noted earlier for various phosphine complexes of some group VIII transition metals.[9–13] $[C_5(CH_3)_5]_2Ti$ appears to be the first example of a complex containing a metal outside of group VIII which undergoes such a reversible addition reaction with hydrogen. Halpern[14] has suggested that such oxidative additions of hydrogen demonstrate the carbenoid character of a coordinatively unsaturated d^8 complex. It is gratifying to note that the d^2 species $[C_5(CH_3)_5]_2Ti$ undergoes a similar oxidative addition, in accord with its predicted carbene-like reactivity.[15]

In addition to its reversible interaction with H_2, $[C_5(CH_3)_5]_2Ti$ exhibits a similar reaction with molecular nitrogen. When it is exposed in hexane or toluene solution to N_2 at atmospheric pressure, the instantaneous formation of a dark blue complex is observed. Upon cooling below 0° this color intensifies. When these solutions are cooled to −80°, residual N_2 can be pumped off without loss of complex. The resulting solutions are then found to contain *1* mol of N_2 bound to *2* mol of $[C_5(CH_3)_5]_2Ti$. The coordinated N_2 is quantitatively released under vacuum at room temperature. The formulation of the N_2 complex as a binuclear species is supported by the observation that the stability of the complex is noticeably enhanced at higher concentrations of decamethyltitanocene. We can therefore hypothesize that a dimeric titanocene species is responsible for the coordination of N_2 according to the equilibrium

$$[C_5(CH_3)_5]TiTi[C_5(CH_3)_5] + N_2 \rightleftharpoons [C_5(CH_3)_5]_2TiN_2Ti[C_5(CH_3)_5]_2$$

The intermediacy of this nitrogen complex in N_2 reduction reactions is presently under investigation. The observation of a similar N_2 coordination by an unsubstituted titanocene species is reported upon in an adjacent communication.[16]

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[8] This hydride is formed in the reaction of $C_{10}(CH_3)_{10}CH_2Ti$ with excess hydrogen. It is therefore necessary to stir the resulting solution at room temperature *in vacuo* for *ca.* 3 hr to convert the hydride to decamethyltitanocene.

[9] L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968).

[10] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

[11] A. Sacco, and M. Rossi, *Chem. Commun.*, 316 (1967); *Inorg. Chim. Acta*, **2**, 127 (1968).

[12] W. H. Knoth, *J. Amer. Chem. Soc.*, **90**, 7172 (1968).

[13] For a recent review, see J. Halpern, *Accounts Chem. Res.*, **3**, 386 (1970).

[14] J. Halpern, *Chem. Eng. News*, **44**, 68 (Oct 31, 1966).

[15] H. H. Brintzinger and L. S. Bartell, *J. Amer. Chem. Soc.*, **92**, 1105 (1970).

[16] R. H. Marvich and H. H. Brintzinger, *ibid.*, **93**, 2046 (1971).

[17] NDEA predoctoral fellow.

A Metastable Form of Titanocene. Formation from a Hydride Complex and Reactions with Hydrogen, Nitrogen, and Carbon Monoxide

Sir:

We wish to report on the observation of a $(C_5H_5)_2Ti$ species with very unusual reaction properties which are paralleled only by those of the sandwich compound $[C_5(CH_3)_5]_2Ti$, described in the preceding communication.[1] Whereas attempts to obtain titanocene in general lead to a rearrangement product $(C_{10}H_9TiH)_2$ of rather trivial reactivity,[2] a highly reactive form of the compound is obtained by a route involving previously described hydride complexes of titanocene.[3] We had found earlier that the dimeric, violet hydride complex $[(C_5H_5)_2TiH]_2$ spontaneously converts to a gray-green isomer when kept at room temperature. The same stable, gray-green hydride is available, most conveniently, by simply treating a saturated hexane solution of dimethyltitanocene, $(C_5H_5)_2Ti(CH_3)_2$, with hydrogen gas at 0°.[4] The hydride complex which precipitates quantitatively in the course of *ca.* 30 min is obtained by filtration, without further purification, as a homogeneously grayish green material of extreme air sensitivity. Under Ar, however, the material can be kept at room temperature without noticeable deterioration.

The composition of the complex is established by the identity of its reactions with those of the violet compound $[(C_5H_5)_2TiH]_2$, for instance its thermal decomposition at *ca.* 100° to the green form of "titanocene" according to eq 1, under evolution of 0.5 mmol of H_2 per mmol of Ti.[5]

$$(1/x)[(C_5H_5)_2TiH]_x \xrightarrow[100°]{} {}^1/_2(C_{10}H_9TiH)_2 + {}^1/_2H_2 \tag{1}$$

The only and striking difference between the two isomeric hydrides is the almost complete lack of solubility in ethereal solvents of the gray-green hydride as an intact compound. On the basis of this observation we would tentatively assign a linear polymeric structure involving $H–Ti–(H–Ti)_x–H$ chains to the gray-

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[1] J. E. Bercaw and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **93**, 2045 (1971).

[2] H. H. Brintzinger and J. E. Bercaw, *ibid.*, **92**, 6182 (1970).

[3] J. E. Bercaw and H. H. Brintzinger, *ibid.*, **91**, 7301 (1969).

[4] This reaction is autocatalytic and proceeds satisfactorily only in saturated solutions in which some dimethyltitanocene crystals are present at the gas–liquid interface. In order to obtain pure hydride, the reaction has to be carried out at about 0° and the solution has to be kept well saturated with H_2, for instance by a large surface–volume ratio and by periodic removal of CH_4; otherwise, the product of the hydrogenation reaction will be contaminated with the green dimeric form of titanocene obtained, for example, by K. Clauss and H. Bestian, *Justus Liebigs Ann. Chem.*, **654**, 8 (1962).

[5] Additional reactions supporting the identity of the gray-green hydride are the formation of $(C_5H_5)_2TiCl_2$ and HD with DCl, the formation of the borohydride $(C_5H_5)_2TiBH_4$ with B_2H_6, and the formation of the phosphine complex $(C_5H_5)_2TiH(P(C_6H_5)_3)$ in triphenylphosphine solutions; see J. E. Bercaw, Thesis, University of Michigan, 1971.

green isomer, as opposed to a dimeric structure with TiH_2Ti rings in the violet form.

The ir spectrum of the gray-green hydride isomer is dominated by a strong, broad band at 1140 cm^{-1} which we attribute to an antisymmetric Ti–H–Ti–H stretching mode.[6] The remainder of the spectrum shows no deviations from those of *bona fide* $(h^5\text{-}C_5H_5)_2Ti$ derivatives, thus supporting the assigned structure. At any rate, the complete absence of the characteristic band at 1230 cm^{-1}, which dominates the spectrum of the green titanocene dimer, shows that this degradation product is present, at the most, as a trace impurity.

A compound with properties rather similar to those described above has recently been observed to form, by Martin, *et al.*,[7,8] in the hydrogenation of 1-methylallyltitanocene. It is to be anticipated that forthcoming analytical and ir data for this compound will further substantiate the identity of their material with ours. In addition, it is quite likely that substantial amounts of the gray-green hydride have been obtained before as an admixture in preparations of the green dimer $(C_{10}H_9TiH)_2$.[9]

While the titanocene hydride might be of substantial synthetic utility as an efficient and easily available hydride-transfer agent, our main interest here is the ease with which this hydride precursor generates the elusive species $(C_5H_5)_2Ti$. When the hydride is suspended and stirred in a solvent like diethyl ether, the gray-green solid slowly disappears. In the course of several hours a homogeneous solution is produced at room temperature, simultaneous with the evolution of 0.5 mmol of H_2 per mmol of Ti. The solutions thus obtained must therefore contain a species of composition $(C_5H_5)_2Ti$. That this species is different from the dimer $(C_{10}H_9TiH)_2$ is evident from optical data. The solutions have a fairly nondescript dark color, rather than the intense green color typical of $(C_{10}H_9TiH)_2$ solutions. Furthermore, ir spectra of such solutions do not exhibit the band splittings characteristic of this dimer; rather, a simple metallocene spectrum with only two strong bands at 790 and 1010 cm^{-1} is obtained.[10] Such a toluene solution turns bright green, however, when heated to 100°, and subsequent isolation of pure $(C_{10}H_9TiH)_2$ shows the $(C_5H_5)_2Ti$ species to be a metastable isomer of this compound. Molecular weight determinations in 0.05–0.1 *M* benzene solutions identify this metastable titanocene isomer as a dimer, $[(C_5H_5)_2Ti]_2$, like the more stable $[C_{10}H_9TiH]_2$ isomer. Yet it differs from the latter most dramatically in its modes of reaction. When exposed to CO, an ether solution of $[(C_5H_5)_2Ti]_2$ immediately absorbs CO to form, in essentially quantitative yields, the carbonyl complex $(C_5H_5)_2Ti(CO)_2$.[11] This reaction with CO is irreversible, just as the CO uptake by $[C_5(CH_3)_5]_2Ti$.[1]

As with decamethyltitanocene, reversible uptake of hydrogen occurs when solutions of $[(C_5H_5)_2Ti]_2$ are exposed to hydrogen gas at 1 atm of pressure. While the amounts of H_2 absorbed are not stoichiometric, one can demonstrate the reversible coordination of hydrogen according to equilibrium 2. When toluene or ether solutions of $[(C_5H_5)_2Ti]_2$ are left in contact with D_2 gas for several hours at room temperature, a complete scrambling of deuterium between the gas phase and all the hydrogen positions in $[(C_5H_5)_2Ti]_2$ is observed.[12]

$$[(C_5H_5)_2Ti]_2 + H_2 \rightleftharpoons (2/x)[(C_5H_5)_2TiH]_x \qquad (2)$$

Of particular interest is the reaction of $[(C_5H_5)_2Ti]_2$ with nitrogen. Slightly cooled solutions of $[(C_5H_5)_2Ti]_2$ in ether, upon exposure to nitrogen gas, instantaneously absorb N_2 to form an intensely blue complex. At −80° 1 mmol of N_2 is retained by 1 mmol of $[(C_5H_5)_2Ti]_2$. This coordination reaction is entirely reversible by warming to room temperature, or by evacuation at about −20°. In concentrated solutions of $[(C_5H_5)_2Ti]_2$ in toluene (>0.1 *M*) the complex persists even at room temperature in an atmosphere of N_2. The nitrogen complex can be obtained as a solid by cooling rather concentrated toluene–hexane solutions of the complex to −80°, filtering, washing with butane, and drying under vacuum, all operations being carried out at −80°. The resulting blue-black powder can be stored under N_2 at room temperature without noticeable decomposition. When dissolved in toluene, it will release 1 mmol of N_2 per 2 mmol of Ti into the vacuum upon warming to room temperature.

A nitrogen complex with essentially identical properties has been observed by Shilov, *et al.*,[13] to form as a transient species when THF solutions of $C_{10}H_{10}TiCl_2$ are reacted with 2 equiv of C_2H_5MgBr at −70° in the presence of nitrogen. Undoubtedly, $[(C_5H_5)_2Ti]_2$ occurs as an intermediate in this reaction system. van Tamelen, *et al.*,[14] on the other hand, have described a N_2 complex of titanocene containing *two* N_2 units per dimer molecule, $C_{20}H_{20}Ti_2(NN)_2$. This complex is formed when titanocene—presumably the green form of the dimer—is exposed to N_2 gas for a period of 3 weeks at room temperature. This N_2 complex is thus distinctly different from the one described here, and it would be interesting to ascertain the modes of

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(6) In the corresponding deuteride this band is shifted to 800–850 cm^{-1}. The substantially lower frequency of this absorption, as compared to that of the dimeric hydride, is undoubtedly related to the different modes of coupling in a linear bond array as opposed to that in a four-membered ring.

(7) H. A. Martin, Thesis, Rijksuniversiteit te Groningen, 1967.

(8) H. A. Martin and R. O. de Jongh, *Chem. Commun.*, 1366 (1969).

(9) This possibility is immediately obvious for the method described by Clauss and Bestian from the close similarity of reaction conditions (see ref 4). But even the reduction of titanocene dichloride with sodium naphthalide, described by G. W. Watt, L. J. Baye, and F. O. Drummond, Jr., *J. Amer. Chem. Soc.*, **88**, 1138 (1966), appears to give an admixture of the gray-green hydride to the green dimer. The ir spectrum given by these authors for their reaction product distinctly shows a broad band at 1100–1150 cm^{-1} superimposed on the spectrum of $(C_{10}H_9TiH)_2$. Such an admixture would also explain the much greater air sensitivity of their preparations as compared to those of pure $(C_{10}H_9TiH)_2$, obtained, for instance, by the method described by J. J. Salzmann and P. Mosimann, *Helv. Chim. Acta*, **50**, 1831 (1967). The prolonged heating in toluene involved in this latter procedure is certain to convert any hydride present to the green degradation product.

(10) The ir spectrum was taken with a solution obtained by decomposing the gray-green hydride in toluene. Attempts to isolate $(C_5H_5)_2Ti$ as a solid have so far not yielded a crystalline material. The ir spectra of residues obtained by removal of the solvent are identical with the solution spectra, however.

(11) Reaction of the green dimer with CO affords only rather negligible yields of the dicarbonyl complex: F. Calderazzo, J. J. Salzmann, and P. Mosimann, *Inorg. Chim. Acta*, **1**, 65 (1967).

(12) *Cf.* also similar observations by Martin and de Jongh (ref 8). In addition to a reversible H_2 uptake, this exchange also demonstrates the ease of ring-to-metal hydrogen shifts postulated earlier (ref 2).

(13) A. E. Shilov, A. K. Shilova, and E. F. Kvashina, *Kinet. Katal.*, **10**, 1402 (1969).

(14) E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Åkermark, *J. Amer. Chem. Soc.*, **91**, 1552 (1969); see also E. E. van Tamelen, *Accounts Chem. Res.*, **3**, 361 (1970).

binding for ring and hydrogen moieties in this compound.

The N_2 complex described here, however, is so strikingly similar in composition, stability, and color to that formed from N_2 and decamethyltitanocene[1] that there can be no reasonable doubt about its structural assignment as a *bone fide* $(C_5H_5)_2Ti$ derivative. Formulation of the complex as $(C_5H_5)_2TiN_2Ti(C_5H_5)_2$ is also supported by the ir spectrum of the solid complex. The spectrum exhibits only the plain metallocene bands mentioned above. The lack of an absorption attributable to the coordinated N_2 moiety is unfortunate for our curiosity about the effects of coordination on the strength of the N–N bond, but of course entirely in accord with the symmetry of this structure. The intermediacy of this nitrogen complex in N_2 reduction reactions will be reported upon in a separate communication.

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Studies on Nuclear Magnetic Resonance Contact Shifts Induced by Hydrogen Bonding with Organic Radicals. I. ^1H and ^{13}C Contact Shifts of Protic Molecules in the Presence of the Nitroxide Radical

Sir:

During the last 20 years considerable interest has been manifested in the study of the hydrogen bond (H bond).[1] A great majority of phenomena connected with the H bond can be explained if this bond is considered as describing an interaction in which the electrostatic charge-migration (covalent bond) as well as the short-range repulsion effects are simultaneously important. The fundamental similarity between the H-bond and charge-migration (or charge-transfer or cocovalent bond) interaction has been emphasized.[1c] Recently MO theoretical studies have been performed for various H-bond systems and proved to be successful in producing H-bond energies, charge distributions, and most stable conformations.[2] All these studies are associated with closed-shell molecules. In the present work we are concerned with the H bond between closed-shell and open-shell molecules which has been studied less experimentally and theoretically. We wish to report here preliminary results of nmr contact-shift and MO theoretical studies for the H bonding in the protic molecule–nitroxide radical system.[3]

In order to assess the importance of covalent bonding in the $XH\cdots Y$ H-bonding system, we have studied proton and ^{13}C contact shifts for various proton donor molecules, XH, induced by the presence of di-*tert*-butyl nitroxide (DTBN), the proton acceptor. We have also carried out unrestricted Hartree–Fock (UHF) calculations using Pople's INDO method[4] for the above H-bond system to substantiate the observed contact shifts. The observation of the XH proton contact shift is expected to reflect directly the electron spin density transferred through the H bond from DTBN. This H-bond contact shift will serve as a measure of covalent character or strength of the $XH\cdots Y$ H-bond interaction. In addition, the contact shifts for other protons and carbons in the XH molecule will allow us to see the mode of electron spin distribution in the XH molecule.

We have observed the effect on ^1H and ^{13}C resonance positions of several XH molecules upon addition of increasing amounts of DTBN.[5] The hydroxyl proton of methanol, for example, in CCl_4 experienced an upfield shift and broadening when a small amount of DTBN was added, while methyl protons were almost unaffected. This upfield shift is proportional to the concentration of added DTBN and is more pronounced for a more acidic XH proton such as in phenol. The observed upfield shifts of the XH proton in the various proton donor molecules are plotted against the DTBN concentration (Figure 1).[6]

The upfield shift is most likely caused by the Fermi contact interaction for the XH proton of that fraction of the XH molecule which is specifically H bonded to DTBN. We have also examined the temperature dependence of this upfield shift. The resulting linear dependence of the shift on $1/T$ (Curie law behavior) may be characteristic of the contact shift.[7,8]

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(1) (a) G. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960; (b) D. Hadzi, Ed., "Hydrogen Bonding," Pergamon Press, Oxford, 1959; (c) S. Bratoz, *Advan. Quantum Chem.*, 3, 209 (1966).

(2) K. Morokuma, H. Kato, T. Yonezawa, and K. Fukui, *Bull. Chem. Soc. Jap.*, **38**, 1263 (1965); K. Morokuma and L. Pederson, *J. Chem. Phys.*, **48**, 3275 (1968); P. Kollman and L. C. Allen, *ibid.*, **51**, 3286 (1969); A. S. N. Murthy and C. N. R. Rao, *Chem. Phys., Lett.*, **2**, 123 (1968); W. Adam, A. Grimison, R. Hoffmann, and G. Zuazaga de Ortiz, *J. Amer. Chem. Soc.*, **90**, 1509 (1968), and other recent papers.

(3) To our knowledge, study of the nmr contact shifts of solvent molecules in the presence of organic radicals has been quite limited [see N. A. Sysoeva, A. U. Stepanyants, and A L. Buchachenko, *Zh. Strukt. Khim.*, **9**, 311 (1968)]. Very recently, de Boer, *et al.*, have reported contact shift data for the solvent molecule (tetrahydrofuran) dissolving radical anions: E. de Boer, A. M. Grotens, and J. Smid, *J. Amer. Chem. Soc.*, **92**, 4742 (1970); *Chem. Commun.*, 1035 (1970).

(4) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **90**, 4201 (1968).

(5) Pmr spectra were obtained at various temperatures on a Jeolco high-resolution nmr spectrometer (60 MHz) using TMS as an internal standard. The concentration of all XH molecules was 2.5×10^{-3} *M* in CCl_4 solution. To this solution, DTBN was added drop by drop (from 3.3×10^{-5} to 16.5×10^{-5} *M*) until the XH proton signal was too broad to be observed. Natural-abundance ^{13}C nmr spectra were recorded with a Jeolco C-60HL spectrometer (15.1 MHz) using a complete proton-decoupling technique.

(6) Since the exchange of the proton donor molecules between H-bonded and nonbonded sites is rapid on the nmr time scale, the spectra are time averaged, the various proton resonances being shifted from their normal diamagnetic values by an amount which is proportional to the concentration of the H-bonded species. Thus as DTBN is added, the proton resonances of the XH molecule shift toward the resonance position of the H-bonded species. The relative values of this shift for various XH molecules are of significance in the present study. The relative values of the slope in the linear relation for various XH molecules may approximately correspond to the relative H-bonding contact shifts in this labile molecular interaction.

(7) This temperature dependence of the shift is, of course, partly caused by the temperature dependence of the equilibrium of the H-bond interaction.

(8) In the diamagnetic solution, the XH proton signal is displaced to lower field by H bonding;[1a,b] this usual downfield shift and upfield contact shift occur simultaneously for the present H-bond systems. However, the contact shift appears to be predominant in the observed DTBN-induced shift; addition of a diamagnetic proton acceptor, in place of DTBN, to the solution of the XH molecule had no substantial effect on the XH proton shift. Therefore, DTBN-induced upfield shifts strongly suggest negative electron spin density on the XH proton induced by H bonding with DTBN, although the apparent values of the relative shifts obtained from Figure 1 are not quantitatively related to the relative values of the induced spin densities.