# Communications to the Editor

## Bis(pentamethylcyclopentadienyl)titanium(II). Isolation and Reactions with Hydrogen, Nitrogen, and Carbon Monoxide

*Sir:*

In a previous communication[1] we presented evidence that the presumably highly reactive species $(C_5H_5)_2Ti$ rearranges and deactivates *via* a ring-to-metal hydrogen shift. In order to investigate the reactivity associated with such a titanium(II) intermediate, we have undertaken the synthesis of decamethyltitanocene, $[C_5(CH_3)_5]_2Ti$. In this compound the occurrence of an $\alpha$-hydrogen shift is impossible, even if the ring ligands are $\sigma$ (or $h^1$) bound; this titanocene species might thus be able to retain its reactive configuration. $[C_5(CH_3)_5]_2Ti$ is prepared by the following reaction sequence.

$$[C_5(CH_3)_5]_2TiCl_2 + 2LiCH_3 \longrightarrow [C_5(CH_3)_5]_2Ti(CH_3)_2 + 2LiCl \quad (1)$$

$$[C_5(CH_3)_5]_2Ti(CH_3)_2 \xrightarrow[\text{toluene}]{100^\circ} C_{10}(CH_3)_{10}CH_2Ti + CH_4 \quad (2)$$

$$C_{10}(CH_3)_{10}CH_2Ti + H_2 \xrightarrow[\text{hexane}]{} [C_5(CH_3)_5]_2Ti + CH_4 \quad (3)$$

The dichloride $[C_5(CH_3)_5]_2TiCl_2$ is obtained from sodium pentamethylcyclopentadienide[2] and $TiCl_3$ in THF, subsequent reaction with excess hydrochloric acid, distribution in $H_2O$–$CHCl_3$, and Soxhlet extraction of the chloroform residue, first with hexane[3] and then with $CCl_4$. The dichloride crystallizes from the $CCl_4$ extract in well-shaped, purple-brown needles. The dimethyl derivative $[C_5(CH_3)_5]_2Ti(CH_3)_2$ is obtained from the dichloride by treatment with methyllithium by a procedure described in detail earlier.[4] Both $[C_5(CH_3)_5]_2TiCl_2$ and $[C_5(CH_3)_5]_2Ti(CH_3)_2$ give satisfactory elemental analyses and nmr spectra consistent with their structures. $CDCl_3$–TMS solutions of the two compounds show singlet nmr absorptions at 1.99 and 1.85 ppm, respectively, indicating equivalence of all ring methyl groups. The dimethyl compound exhibits another singlet at −1.00 ppm (upfield from TMS), the intensity of which is in accord with its assignment to the $Ti(CH_3)_2$ moiety.

Heating the yellow dimethyl derivative in toluene to 110° for 4 hr yields, concurrent with the evolution of 1.0 $CH_4$ per titanium, a turquoise compound of composition $C_{10}(CH_3)_{10}CH_2Ti$, which sublimes at 75° ($10^{-3}$ Torr). The composition of this compound, inferred from the stoichiometry of its formation, is confirmed by its mass spectrum with a parent ion at *m/e* 332.[5] $C_{10}(CH_3)_{10}CH_2Ti$ in hexane solution at 0° readily reacts with $H_2$ to yield, *via* a hydride intermediate (see below), decamethyltitanocene, $[C_5(CH_3)_5]_2Ti$. The reaction requires *ca.* 1.0 mmol of $H_2$ and evolves *ca.* 1.0 mmol of $CH_4$ per millimole of starting material when the solution is subsequently stirred under vacuum. By cooling the resulting hexane solution to −90°, filtering, washing with very little hexane at −90°, and drying under vacuum, a red-brown crystalline material is obtained. The identity of this material as $[C_5(CH_3)_5]_2Ti$ is established, apart from the stoichiometry of its formation, by a mass spectrum with a parent ion at *m/e* 318. The appearance, next to the parent peak, of a strong peak with *m/e* 317 indicates that loss of hydrogen is a favored fragmentation pathway. In accord with this, one observes in the *m/e* region 314–316 overlapping metastable peaks attributable to the loss of hydrogen from the ions with mass 317 and 318. It is obvious that $[C_5(CH_3)_5]_2Ti$, while relatively stable to $\alpha$-hydrogen shift at low temperatures, is a rather fragile molecule at the temperatures necessary for volatilization (*ca.* 100°), and under electron impact.

Nmr spectra of freshly prepared solutions of $[C_5(CH_3)_5]_2Ti$ in benzene-$d_6$ or toluene-$d_8$ show a broad peak with a position which varies reversibly from 36 ppm at −90° to 19.6 ppm at +80°. We attribute this observation to a paramagnetic decamethyltitanocene monomer, occurring in a monomer–dimer equilibrium the details of which will be elaborated in a forthcoming full paper.[6]

In contrast to the fair stability of its precursors, $[C_5(CH_3)_5]_2Ti$ cannot be kept at room temperature (under Ar) for extended periods of time without noticeable decomposition. Samples of decamethyltitanocene were therefore stored at −80° in the dark.

A toluene solution of $[C_5(CH_3)_5]_2Ti$ readily absorbs 2 mol of carbon monoxide to form $[C_5(CH_3)_5]_2Ti(CO)_2$. This substance can be purified by sublimation at 80° ($10^{-3}$ Torr); its nmr spectrum exhibits a single absorption at 1.69 ppm, again indicating the equivalence of all ring methyl groups. The ir spectrum shows two carbonyl absorptions at 1930 and 1850 $cm^{-1}$. These frequencies are close to, but even lower than, those observed in $(C_5H_5)_2Ti(CO)_2$, 1975 and 1897 $cm^{-1}$,[7] illustrating the increased electron-donating capability of the titanium center in the decamethyl derivative. While $[C_5(CH_3)_5]_2Ti(CO)_2$ does not lose its carbon monoxide ligands upon heating or evacuation, a reversible interaction is found to occur between $[C_5(CH_3)_5]_2Ti$ and $H_2$. When hexane or toluene

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[1] H. H. Brintzinger and J. E. Bercaw, *J. Amer. Chem. Soc.*, **92**, 6182 (1970).

[2] 1,2,3,4,5-Pentamethylcyclopentadiene was prepared by the method described by L. deVries, *J. Org. Chem.*, **25**, 1838 (1960). As suggested by Dr. A. J. Ashe, III, $CrO_3$ in pyridine was substituted for activated $MnO_2$ in the oxidation of di-*sec*-2-butenylcarbinol to di-*sec*-2-butenyl ketone. Sodium pentamethylcyclopentadienide is obtained by treatment of pentamethylcyclopentadiene with sodium amide in liquid ammonia.

[3] Extraction with hexane removes the more soluble $(C_5(CH_3)_5)TiCl_3$ contaminant. We find that this compound is the only product if the less soluble $LiC_5(CH_3)_5$ is substituted for the sodium salt; *cf.* R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **8**, 287 (1967).

[4] J. E. Bercaw and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **91**, 7301 (1969).

[5] The nmr spectrum of the intermediate $C_{10}(CH_3)_{10}CH_2Ti$, unlike those of the other decamethyltitanocene derivatives investigated, shows nonequivalent ring methyl groups. Its structure remains to be clarified.

[6] The magnetic susceptibility of $[C_5(CH_3)_5]_2Ti$ solutions, determined by the nmr method described by D. F. Evans, *J. Chem. Soc.*, 2003 (1959), and molecular weight determinations in benzene solution indicate such an equilibrium.

[7] F. Calderazzo, J. J. Salzmann, and P. Mosimann, *Inorg. Chim. Acta*, **1**, 65 (1967).

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.

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## 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.