7.[2b] Electrostatic considerations lend support to the notion that hydroxide attack is occurring. The base hydrolysis of $(CH_3)_3N^+CH_2CO_2C_2H_5$ is about 10^3 times faster than that of $(CH_3)_2NCH_2CO_2C_2H_5$, even though steric requirements for the former are greater. The effect of the positive charge on the nitrogen is apparent.[2] It follows, then, that in the case of the chelated ester complex the positive charge of +3 on the complex should greatly enhance attack by hydroxide.

At this point it is appropriate to summarize the conclusions reached pertaining to the reaction of the glycine ester containing complexes with mercury(II) ion. Mercury(II) ion reacts with *cis*-$Co(en)_2(NH_2CH_2CO_2R)X^{2+}$ in aqueous solution to yield a five-coordinate, highly reactive complex. The vacated position in the coordination sphere of the cobalt(III) is taken by the carbonyl oxygen of the ester to yield the chelated ester complex, $Co(en)_2(NH_2CH_2CO_2R)^{3+}$. In the absence of other nucleophiles, water attacks the positive center, the carbonyl carbon, resulting in hydrolysis of the ester and formation of $Co(en)_2(NH_2CH_2CO_2)^{2+}$. The rate of hydrolysis of the chelated ester is extremely rapid in comparison to that for the ester molecule coordinated through the amino group alone. The hydrolysis of the chelated ester is subject to general nucleophilic or general base catalysis.

These conclusions are in support of the mechanism proposed by Bender and Turnquest for the copper(II)-promoted hydrolysis of α-amino esters. These particular cobalt(III) systems cannot, of course, be taken as establishing the mechanism for the copper ion case. In fact, the demonstration of the path discussed here clearly does not preclude the existence of other mechanisms in other systems, even those containing cobalt(III).

Acknowledgment. The support of these investigations by the National Science Foundation is sincerely appreciated.

Concerning the Status of Bis(cyclopentadienyl)titanium

George W. Watt, Lawrence J. Baye, and Frank O. Drummond, Jr.

Contribution from the Department of Chemistry, University of Texas,
Austin, Texas 78712. *Received October 23, 1965*

Abstract: The status of earlier reports on the synthesis and properties of bis(cyclopentadienyl)titanium is reviewed and evaluated. A synthesis *via* reduction of $(C_5H_5)_2TiCl_2$ with $NaC_{10}H_8$ in tetrahydrofuran, and numerous properties of $(C_5H_5)_2Ti$, are reported and discussed.

In 1956, Fischer and Wilkinson[1] reported the synthesis of $(C_5H_5)_2Ti$ by the reaction

$$TiCl_2 + 2NaC_5H_5 \longrightarrow (C_5H_5)_2Ti + 2NaCl \qquad (1)$$

in tetrahydrofuran (THF). When failure to confirm (1) was reported from this laboratory,[2] we were unaware that the work of Fischer and Wilkinson was antedated by a patent application[3] filed in 1953, claiming synthesis of $(C_5H_5)_2Ti$ *via* reaction 1, but without evidence supporting the identity of the product. We also overlooked the reported synthesis of $(C_5H_5)_2Ti$ by reaction 2 in hexane[4]; the product was characterized only by an

$$(C_5H_5)_2Ti(CH_3)_2 + H_2 \longrightarrow (C_5H_5)_2Ti + 2CH_4 \qquad (2)$$

analysis for titanium.

Levy[5] has stated that $(C_5H_5)_2Ti$ has been prepared only by Fischer and Wilkinson and by Long, both *via* (1). In the latter instance, however, the analytical and other data obtained are not convincing although the identity of the product was assumed.[6] Another laboratory[7] has been unable to verify the results of Fischer and Wilkinson. Also with regard to prior work, Vol'pin, *et al.*,[8] have reported the synthesis of the stable adduct $(C_5H_5)_2Ti(C_6H_5C{\equiv}CC_6H_5)_2$ by addition of $TiCl_4$ and $C_6H_5C{\equiv}CC_6H_5$ to a THF solution of NaC_5H_5. Still more recently, Yokokawa and Azuma[9] reported that they had prepared $(C_5H_5)_2Ti$ by the reaction

$$(C_5H_5)_2TiCl_2 + 2NaHg \longrightarrow (C_5H_5)_2Ti + 2NaCl + Hg \qquad (3)$$

using 1% sodium amalgam in dry toluene; the product of (3), however, was neither isolated nor characterized.

In part because of widespread theoretical speculation[10–17] about the structure of compounds of this type and the obvious need to re-examine the unexpected diamagnetism of $(C_5H_5)_2Ti$, we have continued our work on this compound and report here a synthesis in high yield by the reaction

$$(C_5H_5)_2TiCl_2 + 2NaC_{10}H_8 \longrightarrow (C_5H_5)_2Ti + 2C_{10}H_8 + 2NaCl \qquad (4)$$

under an inert atmosphere in THF at 25°. The results given below show that the product initially crystallized

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from benzene is of high purity that is improved only slightly by sublimation. The latter is slow and it was observed that after the cold surface became entirely covered with the green crystals, their removal was necessary before further deposition would occur.

It must be recognized that the most unusual reactivity of this compound imposes severe limitations upon the kinds of experiments that can be done with it. Its reactivity simply cannot be over-emphasized, particularly in the form initially obtained from solution; the resublimed product was noticeably less reactive.

In the infrared spectrum, the absence of absorption bands in the 2000-cm^{-1} region appears to eliminate the possibility of Ti–H bonds. Otherwise this spectrum (Figure 1) is of interest because of its similarity[18,19] to those of $(C_5H_5)_2Fe$ and $(C_5H_5)Ni$. The most intense band for $(C_5H_5)_2Fe$ and $(C_5H_5)_2Ni$ (CH bend $\perp$) appears at 811 and 773 cm^{-1}, respectively; the corresponding band for $(C_5H_5)_2Ti$ is at 784 cm^{-1}. All three have a shoulder on the high-energy side of this band. The range of frequencies corresponding to motion within the cyclopentadienyl rings is much smaller than the range of those involving the motion of rings with respect to the central metal. For example, the CH bending ($\parallel$) mode appears at 1002, 1000, and 1015 cm^{-1} for the metallocenes of Fe, Ni, and Ti, respectively. On the other hand, the antisymmetric metal–ring vibration which gives a measure of the magnitude of the interaction between the metal and the aromatic ring appears at 478, 355, and 410 cm^{-1}, also respectively. The most noteworthy difference in these spectra is in the vicinity of 1700 cm^{-1}. Both $(C_5H_5)_2Fe$ and $(C_5H_5)_2Ni$ have five bands in this general region in which $(C_5H_5)_2Ti$ shows no absorption. In the latter, however, three bands at 1232, 1262, and 1302 cm^{-1} suggest a shift of all five bands in the $(C_5H_5)_2Ti$ spectrum to lower energies, with two being obscured by absorption attributable to Nujol.

Bis(cyclopentadienyl)titanium is considerably more stable thermally than reported earlier.[1] When the green crystals are heated to near 200° at atmospheric pressure, they turn black and appear to decompose. This black solid, however, dissolves completely in benzene to form a solution from which green $(C_5H_5)_2Ti$ can be recrystallized without evidence for the presence of decomposition products. Also in contrast to an earlier report,[1] we find that $(C_5H_5)_2Ti$ reacts very vigorously with oxygen-free water.

The synthesis procedure described in detail below is currently being extended to other compounds of the type $(C_5H_5)_2M$ where, for example, M = Zr, Hf, Mo, W, or a lanthanide.

Experimental Section

Materials. With the following exceptions, all chemicals employed were reagent grade.

Tetrahydrofuran was purified by distillation over either $LiAlH_4$ or sodium benzophenone. Benzene was distilled over $LiAlH_4$ or Na–K alloy. Both solvents thereafter were protected from exposure to the atmosphere.

Analytical Methods. All transfers of $(C_5H_5)_2Ti$ and preparation of solutions thereof were done in a drybox containing a He atmosphere maintained oxygen and water free by continuous exposure to liquid Na–K alloy.

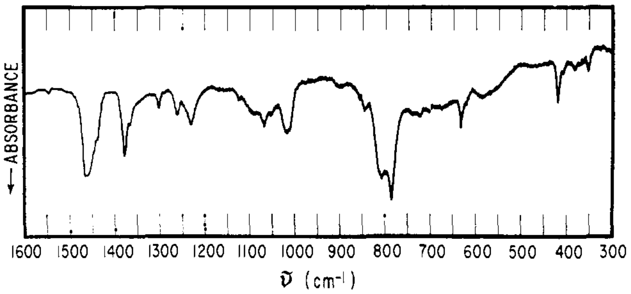

Figure 1. The infrared spectrum of *ca.* 0.02 *M* $(C_2H_5)_2Ti$ in Nujol.

Titanium was weighed as TiO_2 following oxidation of $(C_5H_5)_2Ti$ at controlled rates, first at room temperature and finally at elevated temperatures.

After it was established that carbon and hydrogen could not be determined reproducibly by conventional methods, $C_5H_5^-$ was determined by a modification of a method previously described.[20] The modifications involved cleavage of $(C_5H_5)_2Ti$ (to generate NaC_5H_5) with excess sodium methoxide in methanol rather than potassium in liquid ammonia. Thereafter the reaction mixture was cautiously exposed to air to produce TiO_2 which was removed by filtration and washed with methanol. In the chloromercuration procedure,[20] HgO was substituted for $NaC_2H_3O_2$, and the reaction mixture was allowed to stand for 1 day. Following acidification with dilute acetic acid, $C_5H_5^-$ was weighed as $C_5(HgCl)_6$.

Synthesis. In a dry oxygen-free helium atmosphere, 9.46 g (38 mmoles) of $(C_5H_5)_2TiCl_2$ was added to 1.75 g (76 mmoles) of Na and *ca.* 11 g of $C_{10}H_8$ (*ca.* 10% mole excess) in 100 ml of THF in a 250-ml flask. During stirring for 24 hr the solution assumed a dark green color. The solvent was removed under reduced pressure and the residue was extracted with dry benzene to give a green solution. Removal of the benzene under reduced pressure followed by sublimation of $C_{10}H_8$ at *ca.* 10^{-2} mm and 100° provided 6.1 g [90% yield based on $(C_5H_5)_2TiCl_2$] of small dark green, chlorine-free, *pyrophoric* crystals, mp >200° dec. *Anal.* Calcd for $(C_5H_5)_2Ti$: Ti, 26.90; $C_5H_5^-$, 73.10. Found: Ti, 27.30; $C_5H_5^-$, 73.15. Sublimation at *ca.* 10^{-2} mm and >140° gave larger and somewhat less reactive green crystals. *Anal.* Found: Ti, 27.20; $C_5H_5^-$, 73.08. The molecular weight found (cryoscopically in C_6H_6) was 346, as compared with 178 for the monomer.

Properties. X-Ray diffraction patterns were obtained using Cu Kα radiation, Ni filter, 35 kv, 15 ma, and exposure times of 10–12 hr. With the exception of seven very weak lines, the resulting *d* spacings (A) and relative intensities (I/I_0, in parentheses) for $(C_5H_5)_2Ti$ were: 9.3 (0.5), 6.9 (0.8), 5.6 (0.9), 5.3 (0.9), 4.64 (1.0), 3.60 (0.5), 2.62 (0.2), 2.31 (0.2), 1.99 (0.2), 1.90 (0.2), and 0.84 (0.2).

Magnetic susceptibility was determined at 25° with a modified Curie–Cheneveau balance calibrated against $HgCo(SCN)_4$. All samples of $(C_5H_5)_2Ti$ examined were diamagnetic. In efforts to secure an esr spectrum using a Varian Associates V-4502 spectrometer (100-kc field modulation), no signal was obtained with solid $(C_5H_5)_2Ti$, thus confirming the diamagnetism.

The infrared spectrum (Figure 1) of a *ca.* 0.02 *M* Nujol mull of $(C_5H_5)_2Ti$ was obtained over the 250–4000-cm^{-1} region with a Beckman IR-7 spectrophotometer and a CsI interchange. Owing to the extreme reactivity of the compound, Nujol was the only mulling agent in which a reproducible spectrum could be obtained. Efforts to secure spectra for the ultraviolet and visible regions were unsuccessful because solutions necessarily very dilute could not be protected from oxidation for a sufficiently long time.

An unusually wide variety of solvents was investigated during efforts to obtain an nmr spectrum, but these experiments were of no avail because of interference by the solvent, insolubility of $(C_5H_5)_2Ti$, or (in most cases) reaction between $(C_5H_5)_2Ti$ and the solvent.

Bis(cyclopentadienyl)titanium is very soluble in benzene, toluene, and THF, somewhat less soluble in cyclohexane and *n*-hexane, and highly reactive toward other solvents including water, carbon disulfide, halogenated solvents such as carbon tetrachloride and

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chloroform, liquid sulfur dioxide, dioxane, dimethyl sulfide, dimethyl sulfoxide, and nitromethane. The titanium compound reacts with HCl gas in dry benzene to form a purple solution from which the expected $(C_5H_5)_2TiCl_2$ could not be isolated.

Acknowledgment. This work was supported by the Robert A. Welch Foundation and the U. S. Atomic Energy Commission.

Nuclear Magnetic Resonance in Polycyclic Compounds. II. Long-Range H^1–H^1 and H^1–P^{31} Coupling in Some Adamantane and Bicyclo[2.2.2]octane Derivatives[1a,b]

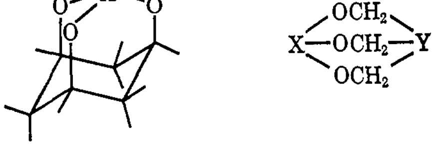
E. J. Boros, K. J. Coskran, Roy W. King, and J. G. Verkade

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa.
Received September 10, 1965

Abstract: The proton nmr spectra of fourteen polycyclic compounds of the types $X(OCH)_3(CH_2)_3$ (where X = HC (I), X = P (II), and X = O=P (III)) and $X(OCH_2)_3Y$ (where X = HC, Y = CCH_3 (IV); X = P, Y = CCH_3 (V); X = O=P, Y = CCH_3 (VI); X = HC, Y = CH (VII); X = P, Y = CH (VIII); X = O=P, Y = CH (IX); X = HC, Y = P (X); X = HC, Y = P=O (XI); X = P, Y = P (XII); and X = O=P, Y = P=O (XIII)) were examined for evidence of long-range spin–spin coupling. Unexpectedly large four-bond POCCH phosphorus–proton couplings were observed for VIII and IX (7.2 and 6.2 cps, respectively) as well as PCOCH phosphorus–proton couplings in X and XI (1.0 and 3.0 cps., respectively). Five-bond HCOCCH proton–proton couplings unprecedented in saturated systems were recorded for I and VII (1.25 and 1.7 cps., respectively). The observed four- and five-bond couplings are discussed in terms of possible through-bond and through-space mechanisms. Syntheses for the new compounds VII, VIII, IX, X, and XI are reported.

The first paper in this series[1a] contained a report of the three-bond POCH coupling constants for various Lewis acid adducts of 2,8,9-trioxa-1-phosphaadamantane (II) and 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (V). Recent reviews of P^{31} nmr spectra[2,3] reported no four-bond phosphorus–proton coupling constants. Values for J_{POCCH} in polycyclic systems reported in this work are up to 15 times larger than values observed in open-chain trialkyl phosphites.[4] Because of the relatively small degree of s character in bonding orbitals of phosphorus, factors other than the Fermi contact interaction may be important in describing phosphorus–hydrogen coupling.[5] In an effort to reveal the effect of molecular geometry on such spin interactions, the proton nmr spectra of the phosphorus compounds II, III, V, VI, and VIII–XIII shown in Figure 1 were studied.

Many four-bond proton–proton coupling constants in saturated systems are known and are the subject of a recent review article.[6] No five-bond proton–proton spin couplings have been reported for saturated systems. In view of a through-space mechanism suggested for four-bonded proton–proton interactions,[7] proton nmr spectra were obtained for I, IV, VII, X, and XI. Although four-bond and six-bond proton–proton couplings were negligible or unobservable in these compounds, appreciable five-bond interactions were observed in I and VII.



	X
I	H-C
II	P
III	O=P

	X	Y
IV	H-C	CCH_3
V	P	CCH_3
VI	O=P	CCH_3
VII	H-C	C-H
VIII	P	C-H
IX	O=P	C-H
X	H-C	P
XI	H-C	P=O
XII	P	P
XIII	O=P	P=O

Figure 1. Structures and formulations of the compounds whose nmr spectra were studied.

Experimental Section[8]

Solvents. All solvents were reagent grade and were dried over Linde 4-A Molecular Sieve. Trimethyl orthoformate was purified by distillation from anhydrous magnesium sulfate and the constant-boiling fraction stored over Linde 4-A Molecular Sieve.

Measurements. Proton nmr spectra were obtained on 5 to 20% by weight solutions on a Varian HR-60 nmr spectrometer operating at 14,100 gauss. The solvent used in all cases was carbon tetrachloride except where indicated. Infrared spectra in the sodium

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