reaction time. With long reaction periods, **3** became the dominant species and the amount of **1d** became comparable to that of **1b** and **1c**. With short reaction periods, the relative amounts of **1b** and **1c** were much larger than those of **1d** and **3**.

To evaluate the catalytic activity of **3** and other possible decomposition products, the following materials were prepared: (1) osmium metal by the high-temperature (550 °C) pyrolysis of $Os_3(CO)_{12}$; (2) pyrolytic decomposition of **1a** at 250 °C; (3) PPN-**3**.[15] These three materials were tested for catalytic tertiary amine metathesis with reaction mixtures and under conditions similar to those employed for the solutions of **1a**. The results listed in Table II were negative in each case. However, suspecting that the PPN counterion of **3** was a poor substitute for the anticipated R_3NH^+ ions in the decomposed solutions of **1a**, an additional test with a catalyst prepared from 1:1 mixture of PPN-**3** and $[Me_3NH]Cl$ was performed. Surprisingly, this catalyst mixture had substantial activity and produced tertiary amine metathesis at a rate of 13.4 turnovers/h. $[Me_3NH]Cl$ was tested separately and was found to be inactive. It was found that solutions of **4** in NEt_3 solvent were converted essentially quantitatively to Et_3NH-**3**, and solutions of **4** in the mixed-amine reaction solutions exhibited an activity for catalysis that is essentially the same as the mixtures of PPN-**3** + Me_3NHCl. This finding rules out the Cl^- ion as being important to the catalysis of the mixture of PPN-**3** and $[Me_3NH]Cl$.

The formations of **1b–d** from the solutions of **1a**, NEt_3, and $NPr_3{}^n$ and of **1c** from **1b** plus $NPr_3{}^n$ clearly show that the carbene complexes are capable of performing the catalysis, but since we found it impossible to perform catalysis with the carbene complexes without the formation of some **3**, we have had to use the results of noncatalytic reactions to obtain estimates of the relative reactivity of the carbene complexes toward the tertiary amines. These evaluations were obtained in the following way. The reaction of **1a** with $NPr_3{}^n$ at 145 °C produced a 56% conversion to **1c** in a period of 30 min. If the reaction continued at that rate for 1 h, then the conversion to **1c** would be 112%, or in terms of TOF, 1.12. The reaction of **1b** with $NPr_3{}^n$ at 145 °C produced only an 11% yield of **1c** in 1 h. The corresponding TOF for the formation of NEt_2Pr^n from **1b** is 0.11. In this way, it is estimated that the potential for catalysis by the carbene complexes is only about 0.8–8.0% of the catalytic activity of **3**. The observed activity of **3** is sufficient to account for the bulk of the tertiary amine metathesis observed in the solutions that were initiated with **1a**. There was no evidence for formation of **1b** or **1c** in metathesized solutions of NEt_3 and $NPr_3{}^n$ when **3** or **4** was used as the catalyst precursor. Thus, it is concluded that carbene complexes **1b–d** are not responsible for tertiary amine metathesis by **3** or **4**. We are not prepared to speculate further as to what the mechanism of catalysis by **3** or **4** might be at this time.

Acknowledgment. These studies were supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. We thank Dr. Suning Wang for assistance with the structural analyses. The Brüker AM-500 NMR spectrometer was purchased with funds from the National Science Foundation under Grant No. CHE-8904942.

Supplementary Material Available: Tables of anisotropic thermal parameters and positional parameters for compounds **1a** and **2e** and the mass spectrum of $NBu_2{}^nEt$ obtained from the reaction of partially deuterated **1f** with NEt_3 in CH_3OD (8 pages); listings of observed and calculated structure factor amplitudes for **2e** (13 pages). Ordering information is given on any current masthead page.

Synthesis and Properties of Some Novel Bis(cyclopentadienyl)silyltitanium(III) Complexes

Edmond Samuel,*,† Ying Mu,‡ John Frank Harrod,*,‡ Y. Dromzee,§ and Yves Jeannin§

Contribution from the Laboratoire de Chimie Organométallique de l'ENSCP (URA 403 CNRS), 11 Rue P. et M. Curie, 75005 Paris, France, Department of Chemistry, McGill University, Montreal, Canada H3A 2K6, and Laboratoire de Chimie des Métaux de Transition (UA 419 CNRS), Université P. et M. Curie, 4 Place Jussieu, 75005 Paris, France.

Received October 10, 1989

Abstract: The complexes $Cp_2Ti(SiHRR')L$ [where L = Et_3P, R = H, and R′ = Ph (**5**); L = Me_3P, R = H (**6**), Ph (**7**), and Me (**8**), and R′ = Ph] have been prepared as crystalline solids by the reaction of Cp_2TiMe_2 with the appropriate silane in the presence of the phosphine ligand. X-ray structures of **5** and **7** were determined. **7** gave a high-quality structure [$R_W = 0.030$, monoclinic, $P2_1/n$, $a = 8.743$ (1) Å, $b = 26.192$ (5) Å, $c = 10.289$ (2) Å, $\beta = 100.97$ (1)°, Ti–P = 2.609 (1) Å, Ti–Si = 2.652 (1) Å, Si–Ti–P = 84.8 (1)°]. The structure of **5** was also determined [$R_W = 0.050$, orthorhombic, $P2_12_12_1$, $a = 8.312$ (4) Å, $b = 14.994$ (5) Å, $c = 17.451$ (4) Å], and the refined molecular parameters were indistinguishable from those of **7**. All of the compounds are paramagnetic monomers. Their isotropic EPR spectra in toluene were measured. In each case hyperfine coupling of the unpaired electron to ^{47}Ti, ^{49}Ti, ^{32}P, and ^1H was resolved.

Silyl complexes of the transition elements have attracted interest for many years because of the group analogy between carbon and silicon and because of the effectiveness of certain transition-metal compounds as catalysts for hydrosilylation reactions.[1-4] Early investigations concerned mostly the silyl complexes of electron-rich transition elements because of the relative ease of their preparation. More recently, a few studies have appeared on compounds of groups 4 and 5 that demonstrate the relevance of such compounds to the catalytic dehydrogenative coupling of organosilanes[5-8] and

---

[†] Laboratoire de Chimie Organométallique de l'ENSCP.

[‡] McGill University.

[§] Université P. et M. Curie.

(1) Speier, J. *Adv. Organomet. Chem.* **1979**, *17*, 407.

(2) Harrod, J. F.; Chalk, A. J. *Metal Carbonyls in Organic Synthesis*; Pino, P., Wender, I., Eds.; Wiley Interscience: New York, 1977; p 673.

(3) Cundy, C. S.; Kingston, B. M.; Lappert, M. F. *Adv. Organomet. Chem.* **1973**, *11*, 253.

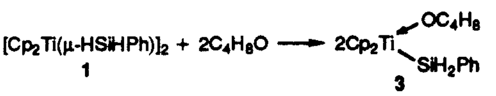
(4) Tilley, T. D. *Organometallics* **1985**, *4*, 1452, and references therein.

0002-7863/90/1512-3435$02.50/0 © 1990 American Chemical Society

as silicon analogues of carbene and carbyne complexes.[9]

In the case of titanium it is well-known that the species responsible for many catalytic reactions are low-valent compounds containing metal–alkyl bonds. However, these have rarely been thoroughly identified, at least from the structural point of view. It is evident that the difficulty in isolating such compounds and their effectiveness as catalysts are related. Similarly, the paucity of examples of silyltitanium complexes and the exceptional catalytic activity of titanocene derivatives for dehydrocoupling are both undoubtedly related to the lability of the Ti–Si bond.

In an earlier report[6] we described the synthesis and characterization of the bimetallic Ti(III)–silyl complexes [$Cp_2Ti(\mu$-$HSiHPh)]_2$ (**1**), and [$Cp_2Ti(\mu$-H)(μ-HSiHPh)$TiCp_2$] (**2**), (Cp = η^5-C_5H_5). Compound **1** was found to react with tetrahydrofuran (THF, OC_4H_8) to give a highly unstable, paramagnetic species, which on the basis of its EPR spectrum was presumed to be the monomeric THF complex [$Cp_2Ti(SiH_2Ph)(THF)$] (**3**), as shown in eq 1. Because of its instability, **3** could not be isolated as a solid. However, the easy cleavage of **1** by the weak donor ligand THF suggested the possibility that stable complexes might be obtained by using other stronger nucleophiles. In this paper we report the synthesis, characterization, and structure determination of some stable phosphine analogues of **3**.



$$[Cp_2Ti(\mu\text{-}HSiHPh)]_2 + 2C_4H_8O \longrightarrow 2Cp_2Ti(\leftarrow OC_4H_8)(SiH_2Ph) \quad (1)$$

1 **3**

Experimental Section

All manipulations were performed under argon with solvents purified and dried by the usual methods. Dimethyltitanocene was prepared by a literature procedure,[10] as was 1,2-diphenyldisilane.[11] Other silanes were purchased from Petrarch Systems Inc. and used as received.

For all of the syntheses described below, the choice of solvent is critical. The best reaction medium is a saturated hydrocarbon, such as pentane or hexane. However, the quality of the crystals can sometimes be improved by the addition of a small amount of aromatic hydrocarbon. Too much aromatic hydrocarbon can lead to failure to the complex to crystallize because of excessive solubility. All of the compounds described in this work decomposed when put in solution, so that purification by recrystallization was prohibited. Analyses had to be performed on crystals obtained directly from the reaction. Even purified transition-metal organosilicon compounds give often unsatisfactory analyses.[12-14]

Preparations of Silyl Compounds 5 and 6: $Cp_2Ti(PEt_3)(SiH_2Ph)$ (5); $Cp_2Ti(PMe_3)(SiH_2Ph)$ (6). In a typical experiment, dimethyltitanocene (500 mg, 2.4 mM) was dissolved in hexane (50 mL) containing PEt_3 (0.42 g, 3.5 mM) and $PhSiH_3$ (0.5 mL). The solution was allowed to stand in daylight.[15] After a while, gas evolution took place accompanied by a progressive color change to dark violet and slow formation of needle-shaped crystals. The gas was collected and shown by IR analysis to be methane. The crystals were separated from the solution and washed with hexane to yield the pure compound **5** (850 mg, 88%). Anal. Calcd for $C_{22}H_{32}PSiTi$: C, 65.35; H, 7.92. Found: C, 63.97; H, 7.80. Compound **6** was prepared under conditions identical with those used for **5**. In this case, the product was obtained as a microcrystalline purple solid.

Table I. EPR Parameters for Some Silyltitanocene Phosphine Complexes. Hyperfine Coupling Constants in Gauss (1 G = 0.1 mT)

compound	$A(P)$	a(H)	A(Ti)	g(iso)
$Cp_2Ti(PEt_3)SiH_2Ph$	29.8	3.1	8.7	1.9968
$Cp_2Ti(PMe_3)SiH_2Ph$	29.3	3.2	8.7	1.9944
$Cp_2Ti(PMe_3)SiHMePh$	29.0	2.9	8.0	1.9966
$Cp_2Ti(PMe_3)SiHPh_2$	29.9	2.6	8.3	1.9976
$Cp_2Ti(PMe_3)SiHPhSiH_2Ph$	28.8	3.2	7.6	1.9959

Table II. Summary of Crystal Data, Intensity Collections, and Structure Refinement Parameters for **5** and **7**

	5	**7**
formula	$TiSiPC_{22}H_{32}$	$TiSiPC_{25}H_{30}$
fw	403	437
cryst system	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$
a, Å	8.312 (4)	8.734 (1)
b, Å	14.994 (5)	26.192 (5)
c, Å	17.451 (4)	10.289 (2)
β, deg		100.97 (1)
V, Å^3	2,175 (4)	2,310 (1)
Z	4	4
cryst size, mm	0.04 × 0.12 × 0.8	0.08 × 0.40 × 0.44
μ(Mo Kα), cm^{-1}	5.4	5.1
ρ_{calcd}, g/cm^3	1.23	1.26
temp, °C	20	20
radiation (graphite monochromator)	Mo Kα (λ = 0.71069)	
2θ limits, deg	3/50	3/52
scan speed, deg/min	depending upon reflection	6
no. of reflctns collected	2187	3761
no. of reflctns used	532	2237
R	0.049	0.030
R_w	0.050	0.030

Preparations of Secondary Silyl Complexes 7–9. Dimethyltitanocene (50 mg, 0.24 mM) was dissolved in a 1:4 (v/v) mixture of toluene and *n*-hexane containing trimethylphosphine (0.028 mL, 0.34 mM) and diphenylsilane (0.13 mL, 0.72 mM). During a period of several hours, the solution slowly changed color from orange to dark violet with a slow gas evolution and the formation of violet crystals of $Cp_2Ti(PMe_3)(SiHPh_2)$ (**7**). The supernatant liquid was decanted and the crystals were washed several times with hexane (yield: 98 mg, 93%). Anal. Calcd for $C_{25}H_{30}PSiTi$: C, 68.49; H, 6.85. Found: C, 67.55; H, 6.57.

A sample of the methylphenylsilyl complex $Cp_2Ti(PMe_3)(SiHMePh)$ (**8**) was prepared under conditions identical with those described for **7**, using 0.10 mL of phenylmethylsilane instead of diphenylsilane (yield: 79 mg, 88%). Anal. Calcd for $C_{20}H_{28}PSiTi$: C, 63.83; H, 7.45. Found: C, 62.58; H, 7.91. The same method was also used to prepare the phenyl(phenylsilyl)silyl complex $Cp_2Ti(PMe_3)(SiHPhSiH_2Ph)$ (**9**).

EPR Spectra. These were recorded on a Bruker ER 220D spectrometer equipped with an Aspect 2000 computer and an ER 4144 variable-temperature unit. The magnetic field was calibrated with a Bruker BNM 12 gaussmeter. The microwave frequency was measured with a Systron Donner frequency counter.

The solutions for EPR measurements were prepared by dissolving crystalline compounds in toluene at <–20 °C and the measurements were made at –20 °C. If solutions were prepared at room temperature, all of the compounds studied had decomposed before measurements could be made. The coupling constants and g values for the compounds studied are shown in Table I.

X-ray Crystallography. Compound 5. The crystals of **5** were usable, but their low cross section resulted in relatively poor diffraction. No crystals of **6** suitable for X-ray diffraction studies were obtained, despite numerous attempts under different synthesis conditions. A single crystal of **5** (0.04 × 0.12 × 0.8 mm) was sealed under argon in a thin-walled glass capillary. Preliminary Laue and precession photographs led to a monoclinic unit cell. The space group $P2_12_12_1$ was established by systematic absences.

Diffraction measurements were carried out on a CAD-4 diffractometer. Unit cells were determined and refined from 25 randomly selected reflections. Crystal data and data collection parameters are given in Table II. During intensity data collection two standard reflections were measured periodically and showed no apparent variation. Intensities were corrected for Lorentz and polarization effects. Reflections with $I \geq 3(I)$ were used in subsequent calculations.

---

(5) Aitken, C. A.; Harrod, J. F.; Samuel, E. *J. Organomet. Chem.* **1985**, *279*, C11.

(6) Aitken, C. A.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059.

(7) Aitken, C. A.; Harrod, J. F.; Samuel, E. *Can. J. Chem.* **1987**, *64*, 1677.

(8) Corey, J. Y.; Chang, L. S.; Corey, E. R. *Organometallics* **1987**, *6*, 1596.

(9) Strauss, D. A.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 5872.

(10) Bestian, K.; Claus, K. *Justus Liebig's Ann. Chem.* **1962**, *65*, 8.

(11) Aitken, C.; Barry, J.-P.; Gauvin, F.; Harrod, J. F.; Malek, A.; Rousseau, D. *Organometallics* **1989**, *8*, 1732.

(12) Arnold, J.; Shina, D. N.; Tilley, T. D. *Organometallics* **1986**, *5*, 2037.

(13) Rodick, D. M.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 945.

(14) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1987**, *6*, 473.

(15) The initiation of all reactions of silanes with dimethyltitanocene is accelerated by visible light. Although the reactions do proceed in the dark, for synthetic purposes the presence of light reduces the time necessary for the overall reaction to occur.

Table III. Selected Interatomic Distances and Bond Angles for **5** and **7**

compd **5**	compd **7**
Bond Distances, Å	
Ti-Si 2.634 (5)	Ti-Si 2.652 (1)
Ti-P 2.651 (6)	Ti-P 2.609 (1)
Ti-Cp(1) 2.042 (7)	Ti-Cp(1) 2.054 (2)
Ti-Cp(2) 2.051 (7)	Ti-Cp(2) 2.058 (2)
Si-C(11) 1.92 (1)	Si-C(41) 1.918 (3)
	Si-C(31) 1.900 (2)
Bond Angles, deg	
P-Ti-Si 86.2 (2)	P-Ti-Si 84.8 (1)
P-Ti-Cp(1) 107.5 (2)	P-Ti-Cp(1) 107.6 (2)
P-Ti-Cp(2) 105.9 (2)	P-Ti-Cp(2) 106.5 (1)
Ti-P-C(17) 115.5 (7)	Ti-P-C(1) 118.6 (1)
Ti-P-C(19) 113.8 (8)	Ti-P-C(2) 119.7 (1)
Ti-P-C(21) 120.6 (9)	Ti-P-C(3) 113.5 (1)
Ti-Si-C(11) 114.4 (5)	Ti-Si-C(31) 121.3 (1)
Cp(1)-Ti-Cp(2) 135.6 (3)	Ti-Si-C(41) 116.8 (1)
	Cp(1)-Ti-Cp(2) 135.4 (1)

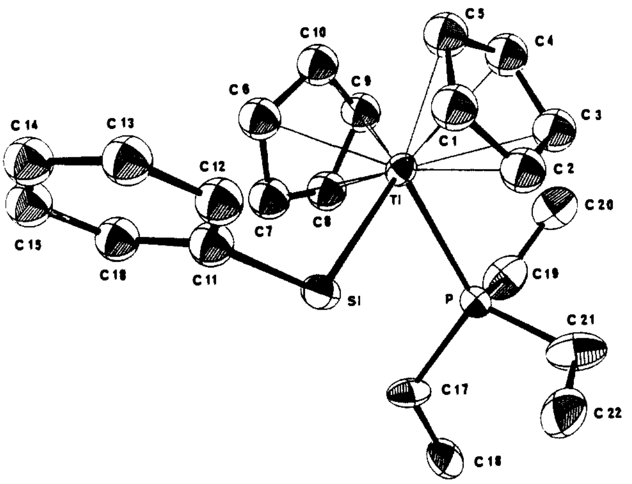


Figure 1. Molecular structure and atom numbering scheme for **5**.

Computations were performed using the CRYSTALS[16] system adapted on a micro VAX-11 computer. The positions of the heavy atoms were deduced from a Patterson map. All other nonhydrogen atoms followed from difference Fourier syntheses. After isotropic refinements of all non-hydrogen atoms an empirical absorption correction was applied by using the program DIFABS.[17] A minimum correction of 0.707 and a maximum correction of 1.157 was employed for 532 observed reflections. This resulted in a diminution of the relative residual from 0.085 before correction to 0.068.

The phenyl ring was fitted to a rigid hexagon (C-C = 139 pm) with overall isotropic thermal parameters for carbon atoms. Cyclopentadienyl rings were fitted to a rigid pentagon (C-C = 140 pm) with overall isotropic thermal parameters for carbon atoms. The hydrogen atoms were calculated and fixed in idealized positions (C-H = 108 pm, Si-H = 150 pm) with refined overall isotropic thermal parameters. Other non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was refined by least squares with approximation (in three blocks) to the normal matrix. Scattering factors were taken from the literature including $\Delta f'$ and $\Delta f''$. In the last stages of refinement, each reflection was assigned a weight $w = w'[1 - \Delta F/6\sigma(F)^2]^2$, where $w' = 1/\sum_n^{r-1} A_r T_r(X)$ with three coefficients A_r(7.408, -7.239, 5.494) for the Chebyshev series $T_r(X)$, where $X = F_c/F_c\text{max}$.[18] The final least-squares calculation converged with residuals as given in Table II. A final difference map showed no residual electron density greater than 0.3 e Å^{-3}. The final atomic coordinates are listed in the supplementary material. Selected bond distances and angles are given in Table III. The molecular geometry and atom numbering scheme are shown in Figure 1.

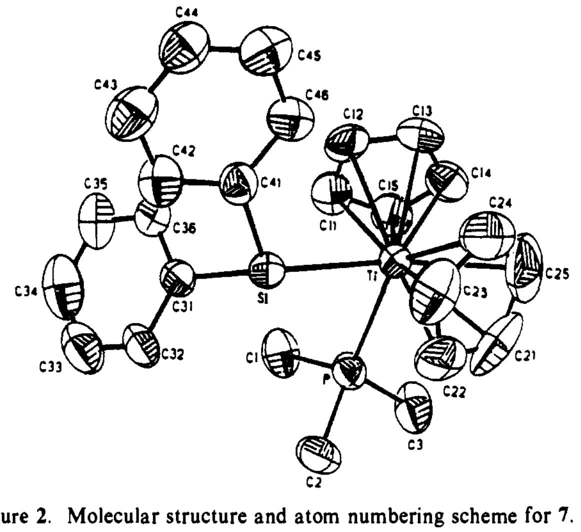


Figure 2. Molecular structure and atom numbering scheme for **7**.

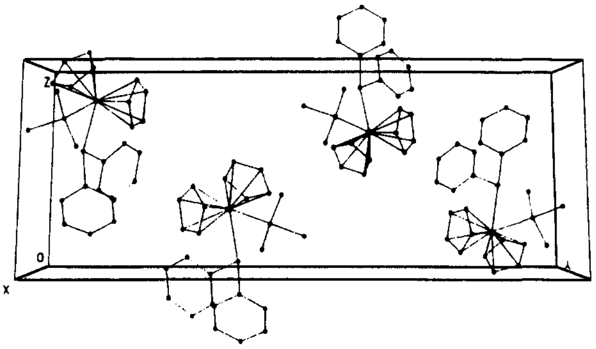


Figure 3. Crystal packing diagram for **7**.

Compound 7.[19] The crystals obtained were of high quality and diffracted excellently. A single crystal of **7** (0.08 × 0.40 × 0.44 mm) was sealed under argon in a thin-walled capillary. Diffraction measurements were carried out on a Nicolet R3M/E diffractometer. Crystal data and data collection parameters are listed in Table II. Computations were performed using the SHELXTL[20] system adapted to an Eclipse S/140 computer. The space group $P2_1/n$ was established by systematic absences in the complete data set ($0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$). The positions of Ti atoms were directly deduced from difference Fourier syntheses and were refined by normal matrix least-squares and isotropic thermal parameters. The hydrogen atoms were calculated by difference Fourier syntheses and fixed in their ideal positions with isotropic thermal refinements. The final atomic coordinates are listed in the supplementary material. Selected bond distances and angles are given in Table III. The final least-squares refinement converged with the residuals shown in Table II. The molecular geometry and atom numbering scheme are shown in Figure 2 and a crystal packing diagram is shown in Figure 3.

Results

Molecular Structures of [Bis(η^5-cyclopentadienyl)(organosilyl)(trialkylphosphine)titanium(III)] Complexes. The molecular structures of **5** and **7** are shown in the form of ORTEP diagrams in Figures 1 and 2. To our knowledge, these are the first examples of structures of Ti(III) complexes containing a simple Ti-M σ bond, where M is a group 14 atom. Although alkyltitanocene(III) complexes have been prepared and their chemistry extensively studied,[21] no X-ray crystallographic study has yet been reported. In addition, the complexes reported herein also appear to be among the rare known examples of paramagnetic silyl complexes.[12-14,22]

---

(16) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. CRYSTALS, Chemical Crystallography Laboratory, University of Oxford, Oxford, England.

(17) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158.

(18) Prince, E. *Mathematical Techniques in Crystallography*; Springer-Verlag: Berlin, 1982.

(19) This crystal structure was purchased from Dr. Zhongsheng Jin of Laboratory 26, Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, PRC.

(20) Sheldrick, G. M. *SHELXTL, an integrated system for solving, refining and displaying crystal structures from diffraction data*, Revision 5; University of Göttingen, Federal Republic of Germany.

(21) See, for example: Klei, E.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *214*, 53, and references therein.

(22) Ol'dekop, Y. A.; Knizhnikov, V. A.; *Zh. Obshch. Khim.* **1981**, *51*, 1723.

Figure 4. EPR spectra at 250 K of (upper) **6** and of (lower) the $PhSiD_2$ analogue, in toluene. Gain, 6; modulation intensity, 0.2 G.

All of the structural features of the complexes conform more or less to expectations. The observed small P–Ti–Si angle is in the range observed for other titanocene(III) complexes.[23] The Ti–Si bond length agrees closely with the values reported for **1** (2.60 and 2.58 Å) and **2** (2.61 Å)[6] and for $Cp_2Ti(SiMe_3)Cl$[24] (2.62 Å). The near identity of the Ti–Si bond lengths in the titanocene(III) and titanocene(IV) species reflects the fact that the unpaired reaction of the Ti(III) compound occupies a nonbonding orbital.[25]

The observed values for the Ti(III)–P bond lengths in this work correspond closely to values reported for other titanocene phosphine complexes in various oxidation states.[26-30]

Steric encumbrance in **5** is minimized by folding of the phenyl group away from the P–Ti–Si triangle and by a helical folding of the three ethyl groups of the phosphine. In this arrangement there are no contacts between substituents of the silyl and the phosphine ligands, or of those ligands with the Cp groups, but the small P–Ti–Si bond angle brings the P and Si atoms very close to van der Waals contact. In **7** one of the phenyl groups occupies more or less the same position as the phenyl group of **5**. The second phenyl group, although much closer to the phosphine ligand, avoids contact by twisting out of the P–Ti–Si plane. However, the unusually large Ti–Si–C(31) angle (121.3°) suggests that some tilting of the diphenylsilyl moiety away from the phosphine is also necessary to avoid excessive steric interaction.

ESR Spectra. All of the complexes described in the present study give well-resolved isotropic EPR spectra in toluene solution. The spectra exhibit hyperfine interaction of the unpaired electron with phosphorus ($I = {}^1/_2$; 100%) and with the α-hydrogens of the silyl ligand, as well as with ^{47}Ti (7.4%) and ^{49}Ti (5.4%) isotopes. The spectrum is diagnostic of the presence of a primary silyl (triplet) or secondary silyl (doublet) group. Figures 4 and 5 show the spectra of **5** and **8** as representative examples. Coupling constants and *g* values for all of the studied complexes are listed in Table I. The assignment of the coupling of the electron to the silyl hydrogen was confirmed by reaction with $PhSiD_3$, which yielded the expected spectrum consisting only of a doublet, due to loss of resolution of the superhyperfine interaction with the deuterium nuclei.

Figure 5. EPR spectrum of **8**. Conditions as in Figure 4.

When trimethyl- or triethylphosphine was added to a solution of **1** in toluene, the color change from blue to violet took place and the same EPR spectra were obtained as with **5** and **6**.

Reactions of Dimethyltitanocene with Primary and Secondary Silanes in the Presence of Phosphines. When dimethyltitanocene reacts with several molar excess of phenylsilane in a hydrocarbon solvent, the reaction mixture turns from orange to intense royal blue in color and eventually precipitates blue-black crystals of **1**.[6] This behavior is unaffected by the addition of an equivalent of triisopropylphosphine, or tricyclohexylphosphine but is completely altered by the addition of an equivalent of trimethyl- or triethylphosphine. In these cases the solution turns deep violet and a product precipitates as dark violet crystals.

The reactions of secondary silanes with dimethyltitanocene resemble those of the primary silanes, in that the color change is the same and dark blue solids precipitate. Yet only for primary silanes, and in particular $PhSiH_3$, have well-defined, crystalline products such as **1** and **2** been obtained. Further, although titanocene-based catalysts can dehydrocouple secondary silanes under forcing conditions, the rates are orders of magnitude slower than the reactions of primary silanes. It is therefore significant that the secondary silyltitanocene phosphine complexes **7** and **8** can be isolated, since this at least confirms that the path of the reactions of primary and secondary silanes is essentially the same up to the production of the silyltitanocene(III) species.

Discussion

The present results provide strong evidence for the existence of the equilibria shown in the following scheme:

$$\underset{\mathbf{a}}{{}^1/_2[Cp_2Ti(SiHRR')]_2} \longrightarrow \underset{\mathbf{b}}{Cp_2Ti(SiHR'R'')} \underset{-PR_3}{\overset{+PR_3}{\rightleftharpoons}} \underset{\mathbf{c}}{Cp_2Ti(SiHR'R'')(PR_3)}$$

The influence of steric bulk of both the silyl and the phosphine ligands is evident. The monomeric complexes (**c**) may be obtained either by direct reaction of primary or secondary silanes with dimethyltitanocene in the presence of a lighter alkylphosphine (e.g., trimethyl or triethyl; cone angles θ = 118 and 132°, respectively[31]) or by cleavage of the dimer (**a**) by such a phosphine. Attempts to prepare **c** with bulkier phosphines, such as triisopropyl, tricyclohexyl-, or triphenylphosphines (θ = 160, 172, and 145°, respectively) were not successful. Moreover, these phosphines did not seem to have any effect on the normal reaction course for the production of the dimers **a**. Other phosphines, such as tri-*n*-bu-

---

(23) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B., Rees, G. V. *Acta Crystallogr., Sect. B* **1974**, *30*, 229.

(24) Rosch, L.; Altnau, G.; Erb, W.; Pickardt, J.; Bruncks, N. *J. Organomet. Chem.* **1980**, *197*, 51.

(25) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(26) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Wolf, B.; Thewalt, W. *J. Organomet. Chem.* **1985**, *297*, 159.

(27) Payne, R.; Hachgenei, J.; Fritz, G.; Fenske, D. *Z. Natuforsch.* **1986**, *41B*, 1535.

(28) Razavi, A.; Mallin, D. T.; Day, R. O.; Rausch, M. D. *J. Organomet. Chem.* **1987**, *333*, C48.

(29) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Honold, B.; Thewalt, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 394.

(30) Girolami, G. S.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 2347.

(31) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

tylphosphine (θ = 132°) clearly, by visual inspection and EPR signals, gave the product **c**, but crystals were not obtained due to high solubility of the products, even in hexane. The species **b** can therefore only be intercepted if the phosphine is not too sterically demanding or too oleophilic. Similar constraints will limit success in obtaining crystalline products from bulky silanes.

The coordinatively unsaturated species **b** is apparently very reactive, as are the alkyltitanocene(III) analogues,[21] and any factor that leads to an increase in its concentration is also likely to lead to decomposition. The facile dissociation of the phosphine ligand at room temperature on dissolution of the pure complexes is the most likely cause of their rapid decomposition. The question of how Ti(III) is formed in these reactions remains an open one. Two routes seem equally plausible at the present time. The first is a homolytical bond cleavage of an unstable Ti(IV) intermediate. The bond involved could conceivably be a Ti–H, a Ti–C, or a Ti–Si bond. A second route would be the conproportionation of titanocene, resulting from a two-electron reduction process such as reductive elimination or two one-electron reduction steps, with a Ti(IV) species. We are continuing to seek further evidence to discriminate between these two possibilities.

Conclusion

The silyltitanocene(III) compounds described above are, to our knowledge, the only examples of structurally characterized mononometallic compounds with a Ti(III)–group 14 bond. Together with the bimetallic species **1** and **2**, they show that there is a rich chemistry of relatively stable silyl species associated with this metal in its oxidation state (III). This situation contrasts with the corresponding carbon chemistry, where alkyl compounds of titanocene(III) are thermally unstable, and no compounds, with or without donor ligands, have been isolated and structurally characterized. Successful isolation of these novel silylphosphine compounds seems to depend largely on the importance of steric interactions of the substituent groups on the silicon and on phosphorus in the molecule. Their reactivity, particularly with respect to understanding the mechanism of titanocene-catalyzed dehydrogenative coupling of silanes, is the subject of further study.

Acknowledgment. Financial support from the Natural Science and Engineering Research Council of Canada and the Fonds FCAR de Quebec is gratefully acknowledged by J.F.H. We are grateful to J. Hênique for technical assistance.

Supplementary Material Available: Tables of fractional atomic coordinates, isotropic and anistropic thermal parameters, bond lengths, bond angles, and least-squares planes for **5** and **7** (16 pages); observed and calculated structure factors for **5** and **7** (20 pages). Ordering information is given on any current masthead page.

Preparative, Structural, and Magnetic Studies of 2-Hydroxypyridinate Complexes of Diruthenium(II)

F. Albert Cotton,[*,1a] **Tong Ren,**[1a] **and Judith L. Eglin**[1b]

Contribution from the Department of Chemistry and Laboratory of Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Department of Chemistry, Michigan State University, East Lansing, Michigan 48824. *Received September 5, 1989*

Abstract: Three new compounds each containing the Ru_2^{4+} core bridged by four 6-X-2-hydroxypyridinate anions (mhp^-, X = CH_3; chp^-, X = Cl; bhp, X = Br) have been prepared in good yields (60–90%) from $Ru_2(O_2CCH_3)_4$, and each one has been characterized by X-ray crystallography and magnetic susceptibility measurements from ca. 5 to ca. 300 K. (**1**) Red-brown $Ru_2(mhp)_4$ crystallizes in space group *Pbca* with a = 16.165 (3) Å, b = 18.638 (5) Å, c = 15.745 (3) Å, V = 4744 (3) Å^3, and Z = 8; (**2**) brown $[Ru_2(chp)_4]_2{\cdot}CH_2Cl_2$ crystallizes in space group $P\bar{1}$ with a = 14.489 (7) Å, b = 15.514 (10) Å, c = 11.703 (2) Å, α = 101.13 (3)°, β = 103.60 (3)°, γ = 100.03 (4)°, V = 2452 (4) Å^3, and Z = 2; (**3**) dark-red $Ru_2(bhp)_4$ crystallizes in space group $P2_1/c$ with a = 14.996 (5) Å, b = 13.464 (6) Å, c = 16.130 (5) Å, β = 109.22 (3)°, V = 3075 (4) Å^3, and Z = 4. The structure of $Ru_2(mhp)_4$ has Ru–Ru = 2.235 (1) Å and a torsion angle of 6.2°, with a symmetrical ligand arrangement placing like atoms (i.e., N's or O's) trans at each end. The $Ru_2(bhp)_4$ molecule is very similar, with Ru–Ru = 2.259 (1) Å and a torsion angle of 1.17°. The chp compound has tetranuclear molecules consisting of two approximately (but not rigorously) identical halves bonded by axial O–Ru bonds. Within each half, three chp ligands are oriented in the same direction. Both Ru–Ru distances are 2.247 (1) Å, and the twist angles are 19.9° and 20.8°, respectively. All three compounds show essentially the same magnetic behavior, indicating that they have a spin-triplet/orbital-singlet ground state derived from a $\delta^{*2}\pi^{*2}$ electron configuration. Zero-field splitting of the state to give a lower singlet ($M_S = 0$) causes the magnetic moment to aproach zero as $T \rightarrow 0$ K.

Although $M_2(xhp)_4$ compounds of other elements were known earlier,[2] the first $Ru_2(xhp)_4$ compound was reported in 1980, namely $Ru_2(mhp)_4$.[3] In fact, this was the first quadruply bridged Ru_2^{4+} complex of any type to be isolated and characterized. While it had been clear since 1975, from the electrochemical study[4] of $Ru_2(O_2CC_3H_7)_4Cl$, that $Ru_2(O_2CR)_4L_2$ compounds should be obtainable, the first one was actually reported only in 1984.[5] Following this, a number of others have been described.[6–9]

---

(1) (a) Texas A&M University. (b) Michigan State University.

(2) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; John Wiley & Sons: New York, 1982. (b) Abbreviations: xhp^- represents a substituted 2-hydroxypyridinate anion with X in the 6-position. mhp^-, chp^-, and bhp^- are the 6-methyl, 6-chloro, and 6-bromo species, respectively.

(3) (a) Berry, M.; Garner, C. D.; Hillier, I. H.; MacDowell, A. A.; Clegg, W. *Inorg. Chim. Acta* **1981**, *53*, L61. (b) Clegg, W. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 3112.

(4) Cotton, F. A.; Pederson, E. *Inorg. Chem.* **1975**, *14*, 388.

(5) Lindsay, A. J.; Tooze, R. P.; Motevalli, M.; Hursthouse, M. B.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1984**, 1383.

(6) Lindsay, A. J.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc. Dalton Trans.* **1987**, *2723*.

(7) Spohn, M.; Strahle, J.; Hiller, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *41*, 541.

(8) Cotton, F. A.; Miskowski, V. M.; Zhong, B. *J. Am. Chem. Soc.* **1989**, *111*, 6177.

0002-7863/90/1512-3439$02.50/0