methylene chloride, and a layer of hexane was floated above this solution. After about 7 days, the hexane layer was bronze colored and began depositing red-brown crystals of $Mo_2Cl_6(DTO)_2$. The compound is air-stable and insoluble in most organic solvents and water.

Crystallographic Study of $Mo_2Cl_6(DTO)_2$. Suitable crystals were obtained by the above procedure. The crystal selected was mounted on the end of a glass fiber. The crystal was examined, data were collected, and the structure was refined following essentially the procedure described above for the other compound. The largest peak in the final difference Fourier was 0.83 e/Å^3. Crystallographic data are listed in Table I. No absorption correction was applied.

Acknowledgment. We are grateful to the Robert A. Welch Foundation for support. J.W.F. thanks Southwest Texas State University for a faculty study leave during the Spring semester, 1978.

Registry No. $Mo_2O_3(C_5H_4NS)_4$, 67583-97-5; $Mo_2Cl_6(DTO)_2$, 67584-20-7; $Mo_2(O_2CCH_3)_4$, 14221-06-8; $Mo_2Cl_4(EtSCH_2CH_2SEt)_2$, 67598-73-6.

Supplementary Material Available: Tables of structure factors for both compounds (10 pages). Ordering information is given on any current masthead page.

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Syntheses and Molecular Structures of Two Metalloindene Complexes: 1,1-Bis(η^5-cyclopentadienyl)-2,3-bis(pentafluorophenyl)benzotitanole and 1,1-Bis(η^5-cyclopentadienyl)-2-trimethylsilyl-3-phenylbenzotitanole

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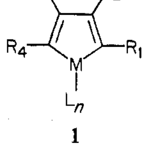
The thermally induced reactions of bis(η^5-cyclopentadienyl)diphenyltitanium with several symmetrical and unsymmetrical acetylenes have been investigated. Two of the products, derived from bis(pentafluorophenyl)acetylene and phenyltrimethylsilylacetylene, have been shown to be 1,1-bis(η^5-cyclopentadienyl)-2,3-bis(pentafluorophenyl)benzotitanole (**7**) and 1,1-bis(η^5-cyclopentadienyl)-2-trimethylsilyl-3-phenylbenzotitanole (**8**), respectively. Their unique metalloindene structures have been unequivocally established (by means of single-crystal X-ray diffraction techniques) with three-dimensional data gathered by counter methods. Orange-red crystals of $(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6F_5)_2$ (**7**) belong to the monoclinic space group $C2/c$ with unit cell constants a = 27.953 (7) Å, b = 14.912 (5) Å, c = 15.783 (5) Å, and β = 119.14 (2)°. The calculated density of 1.52 g·cm^{-3}, assuming eight molecules of **7** and four molecules of hexane of crystallization per unit cell, agrees well with the measured value of 1.50 (3) g·cm^{-3}. Full-matrix least-squares refinement converged with a conventional R factor of 0.070 based on 1993 observed reflections. The Ti–C (σ) bond lengths are 2.132 (10) and 2.219 (9) Å. Crystals of $(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6H_5)[Si(CH_3)_3]$ (**8**) form in the orthorhombic space group $Pbca$ with a = 10.521 (7) Å, b = 15.207 (7) Å, c = 28.636 (7) Å, and ρ_{calcd} = 1.25 g·cm^{-3} for eight molecules in the unit cell. The final R value was 0.032 for 2198 observed reflections. The Ti–C (σ) bond lengths are 2.161 (3) and 2.170 (3) Å.

Introduction

Metallocyclic derivatives of the transition metals have been the subject of considerable research in recent years, both from their possible intermediacy in various homogeneous catalytic processes such as acetylene oligomerization, olefin disproportionation, etc., and from the potential aromaticity of various unsaturated analogues. As part of our continuing research program in metallocycle chemistry, we have recently been able to isolate and carry out X-ray diffraction studies on a variety of metallocyclopentadienes (metalloles) (**1**) containing Ti,[2] Hf,[2] Co,[3] and Rh.[4]



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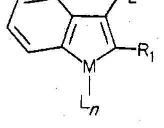

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The present study was undertaken in order to gain analogous structural information on a related series of organometallic compounds, the metalloindenes (**2**), which formally are metallocyclopentadienes containing an unsymmetrically fused benzene ring. Compared to the metallocyclopentadienes **1**, metalloindenes **2** have been considerably less investigated. In the case of transition-metal analogues, the known metalloindenes are presently limited to examples in which the heteroatom is either Ti[5,6] or Mn[7] and a variety of binuclear complexes of Fe,[8-12] Ru,[12] and Os[12] in which the metalloindene ring system is simultaneously coordinated to a $M(CO)_3$ fragment of the same respective metal.

The only X-ray crystallographic investigations on metalloindenes have thus far been conducted on these latter types of complexes containing either Fe (**3**, **4**)[11,13] or Os (**5**).[12] These studies would not necessarily be expected to provide useful structural information relative to the molecular parameters of *non*coordinated metalloindenes, however, since it is known that coordination of a metallocyclic ring to a transition metal considerably perturbs the ring system.[14]

In the present paper, we report on the synthesis, properties,

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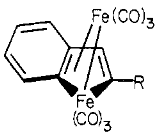
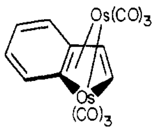
Table I. Crystal Data

	$(C_5H_5)_2TiC_8H_4$-$(C_6H_5)[Si(CH_3)_3]$	$(C_5H_5)_2TiC_8H_4$-$(C_6F_5)_2\cdot{}^1/_2C_6H_{14}$
mol wt	428.5	655.4
linear abs coeff μ, cm^{-1}	4.50	4.25
calcd density, $g\cdot cm^{-3}$	1.25	1.52
obsd density, $g\cdot cm^{-3}$		1.50 (3)
max crystal dimensions, mm	0.28 × 0.55 × 0.70	0.15 × 0.22 × 0.32
space group	orthorhombic, *Pbca*	monoclinic, *C2/c*
molecules per unit cell	8	8
cell constants[a]		
a, Å	10.521 (7)	27.953 (7)
b, Å	15.207 (7)	14.912 (5)
c, Å	28.636 (7)	15.783 (5)
β, deg		119.14 (2)
cell vol, Å^3	4581.6	5746.5

[a] Mo Kα radiation, λ 0.710 69 Å. Ambient temperature of 23 ± 1 °C.



3, R = Ph
4, R = H



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and structures of two new metalloindenes, each containing a single metal atom: 1,1-bis(η^5-cyclopentadienyl)-2,3-bis(pentafluorophenyl)benzotitanole (**7**) and 1,1-bis(η^5-cyclopentadienyl)-2-trimethylsilyl-3-phenylbenzotitanole (**8**). These represent the first X-ray crystallographic determinations of uncoordinated metalloindenes.

Experimental Section

All operations were carried out under an argon atmosphere using conventional Schlenk-tube techniques. The argon was dried over H_2SO_4 and P_2O_5, and trace oxygen was removed using BTS catalyst (BASF). Benzene and hexane were dried over calcium hydride and freshly distilled under argon. Ethyl ether and tetrahydrofuran were predried over sodium and subsequently freshly distilled under argon from sodium–benzophenone. Column chromatography was carried out under argon using Ventron-Alfa neutral-grade alumina. The alumina was heated with a heat gun while mixing on a rotary evaporator attached to a vacuum pump for 2 h to remove water and oxygen. The alumina was then deactivated with 5% (by weight) argon-saturated water and stored under argon until use.

Proton NMR and IR spectra were recorded on Perkin-Elmer R-12A and Beckman IR-10 spectrometers, respectively. Mass spectra were obtained using a Perkin-Elmer Hitachi RMU-6L mass spectrometer. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. All melting points were taken under argon and are uncorrected. Bis(η^5-cyclopentadienyl)diphenyltitanium,[15] bis(pentafluorophenyl)acetylene,[16] and phenyltrimethylsilylacetylene[17] were prepared according to literature methods.

Reaction of Bis(η^5-cyclopentadienyl)diphenyltitanium and Bis(pentafluorophenyl)acetylene. Bis(η^5-cyclopentadienyl)diphenyltitanium (500 mg, 1.5 mmol) and bis(pentafluorophenyl)acetylene (537 mg, 1.5 mmol) were dissolved in 15 mL of anhydrous benzene and refluxed for 1.5 h with magnetic stirring. To the resultant orange-red solution was added ca. 1.0 g of alumina, and the solvent was removed with continuous stirring in vacuo. The residue was added to a column of alumina (2 × 40 cm) which had been packed dry under argon.

Elution with hexane brought down a colorless band containing 190 mg (35% recovery) of unreacted bis(pentafluorophenyl)acetylene. Subsequent elution with 5:1 hexane–benzene removed an additional 11 mg of colorless solid. Analysis of this residue by means of GC/MS techniques showed it to consist of a 4:1 mixture of 1,2-bis(pentafluorophenyl)phenylethene (M^+ 436) and 1,2,3,4-tetrakis(pentafluorophenyl)-1,3-butadiene (M^+ 718).

Table II. Final Fractional Coordinates for 1,1-Bis(η^5-cyclopentadienyl)-2-trimethylsilyl-3-phenylbenzotitanole

atom	*x/a*	*y/b*	*z/c*
Ti	0.13449 (6)	0.47692 (4)	0.33740 (2)
Si	0.03573 (9)	0.33213 (6)	0.43147 (3)
C(1)	0.0025 (3)	0.4206 (2)	0.3873 (1)
C(2)	−0.1150 (3)	0.4564 (2)	0.3810 (1)
C(3)	−0.1358 (3)	0.5279 (2)	0.3465 (1)
C(4)	−0.2529 (3)	0.5714 (2)	0.3420 (1)
C(5)	−0.2658 (4)	0.6402 (2)	0.3106 (1)
C(6)	−0.1651 (4)	0.6653 (2)	0.2833 (1)
C(7)	−0.0493 (4)	0.6220 (2)	0.2871 (1)
C(8)	−0.0315 (3)	0.5528 (2)	0.3186 (1)
C(9)	−0.2309 (3)	0.4254 (2)	0.4069 (1)
C(10)	−0.2685 (4)	0.4649 (3)	0.4481 (1)
C(11)	−0.3738 (5)	0.4339 (5)	0.4722 (2)
C(12)	−0.4418 (5)	0.3676 (6)	0.4550 (3)
C(13)	−0.4096 (5)	0.3282 (4)	0.4137 (3)
C(14)	−0.3026 (4)	0.3583 (3)	0.3899 (2)
C(15)	−0.0385 (5)	0.2250 (3)	0.4150 (2)
C(16)	−0.0155 (5)	0.3624 (3)	0.4919 (2)
C(17)	0.2095 (4)	0.3105 (3)	0.4372 (2)
C(18)	0.1440 (4)	0.3271 (2)	0.3128 (1)
C(19)	0.0471 (4)	0.3661 (3)	0.2872 (1)
C(20)	0.1006 (4)	0.4296 (2)	0.2583 (1)
C(21)	0.2311 (4)	0.4312 (2)	0.2663 (1)
C(22)	0.2584 (4)	0.3677 (3)	0.3006 (1)
C(23)	0.2275 (5)	0.6186 (3)	0.3424 (2)
C(24)	0.3261 (4)	0.5598 (3)	0.3417 (2)
C(25)	0.3182 (4)	0.5079 (3)	0.3824 (2)
C(26)	0.2131 (4)	0.5383 (3)	0.4079 (1)
C(27)	0.1578 (4)	0.6060 (3)	0.3828 (2)
H(1)[C(4)]	−0.329	0.552	0.362
H(2)[C(5)]	−0.349	0.673	0.308
H(3)[C(6)]	−0.175	0.716	0.260
H(4)[C(7)]	0.026	0.641	0.267
H(5)[C(10)]	−0.218	0.518	0.461
H(6)[C(11)]	−0.401	0.463	0.504
H(7)[C(12)]	−0.521	0.345	0.473
H(8)[C(13)]	−0.462	0.275	0.403
H(9)[C(14)]	−0.278	0.327	0.358
H(10)[C(15)]	−0.133 (4)	0.233 (3)	0.423 (1)
H(11)[C(15)]	−0.020 (4)	0.204 (3)	0.384 (2)
H(12)[C(15)]	−0.019 (4)	0.188 (3)	0.439 (1)
H(13)[C(16)]	0.040 (4)	0.326 (3)	0.514 (1)
H(14)[C(16)]	−0.113 (4)	0.346 (3)	0.495 (1)
H(15)[C(16)]	0.007 (4)	0.419 (3)	0.498 (2)
H(16)[C(17)]	0.250 (4)	0.358 (3)	0.455 (1)
H(17)[C(17)]	0.222 (4)	0.263 (3)	0.459 (1)
H(18)[C(17)]	0.244 (4)	0.300 (3)	0.410 (1)
H(19)[C(18)]	0.134	0.278	0.337
H(20)[C(19)]	−0.047	0.351	0.289
H(21)[C(20)]	0.051	0.469	0.235
H(22)[C(21)]	0.296	0.471	0.250
H(23)[C(22)]	0.345	0.351	0.314
H(24)[C(23)]	0.208	0.664	0.316
H(25)[C(24)]	0.394	0.555	0.316
H(26)[C(25)]	0.377	0.458	0.391
H(27)[C(26)]	0.079	0.642	0.392
H(28)[C(27)]	0.179	0.652	0.352

Further elution with 1:1 hexane–benzene developed a light orange band. This band was collected and the solvent removed in vacuo to produce 229 mg (25%) of 1,1-bis(η^5-cyclopentadienyl)-2,3-bis(pentafluorophenyl)benzotitanole (**7**). An analytical sample, mp 237–238 °C, was obtained by recrystallization from ethyl ether–hexane and subsequent drying in vacuo at room temperature.

Proton NMR τ (C_6D_6) 4.15 (10 H, s, η^5-C_5H_5), 3.0–3.5 (4 H, m, C_6H_4); IR (KBr) 1510 (s), 1475 (s), 1310 (m), 1100 (w), 975 (s), 810 (s), 755 (m), 715 (m) cm^{-1}; mass spectrum *m/e* (%) 612 (92, M^+), 593 (2, $(M - F)^+$), 358 (8, $(C_6F_5C_2C_6F_5)^+$), 354 (4, $(C_{10}H_{10}TiC_6F_5)^+$), 178 (42, $(C_{10}H_{10}Ti)^+$), 132 (100, $(C_5H_5FTi)^+$), 113 (54, $(C_5H_5Ti)^+$). Anal. Calcd for $C_{30}H_{14}F_{10}Ti$: C, 58.84; H, 2.29; Ti, 7.82. Found: C, 58.69; H, 2.16; Ti, 7.86.

Final elution of the column with 3:3:1 hexane–benzene–tetrahydrofuran produced two minute golden yellow bands which were not characterized, followed by an additional 8 mg of 1,2-bis(pentafluorophenyl)phenylethene (total yield 17 mg).

Table III. Anisotropic Thermal Parameters[a,b] for the Nonhydrogen Atoms of 1,1-Bis(η^5-cyclopentadienyl)-2-trimethylsilyl-3-phenylbenzotitanole

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ti	0.00798 (5)	0.00308 (1)	0.00099 (1)	−0.00027 (4)	0.00031 (2)	−0.00015 (1)
Si	0.00899 (9)	0.00306 (4)	0.00111 (4)	0.00029 (6)	−0.00017 (3)	0.00018 (2)
C(1)	0.0083 (3)	0.0029 (2)	0.0010 (1)	−0.0001 (2)	0.0002 (1)	−0.0001 (1)
C(2)	0.0086 (3)	0.0032 (2)	0.0009 (1)	0.0001 (2)	0.0001 (1)	−0.0001 (1)
C(3)	0.0098 (3)	0.0032 (1)	0.0009 (1)	0.0007 (2)	−0.0000 (1)	−0.0001 (1)
C(4)	0.0104 (4)	0.0047 (2)	0.0011 (1)	0.0017 (2)	−0.0002 (1)	−0.0000 (1)
C(5)	0.0143 (5)	0.0050 (2)	0.0014 (1)	0.0033 (3)	−0.0002 (1)	0.0002 (1)
C(6)	0.0174 (6)	0.0044 (2)	0.0014 (1)	0.0022 (3)	−0.0003 (2)	0.0003 (1)
C(7)	0.0142 (5)	0.0042 (2)	0.0011 (1)	0.0001 (2)	0.0005 (1)	0.0003 (1)
C(8)	0.0108 (4)	0.0030 (2)	0.0010 (1)	0.0001 (2)	0.0003 (1)	−0.0000 (1)
C(9)	0.0076 (4)	0.0045 (2)	0.0014 (1)	0.0006 (2)	−0.0002 (1)	0.0005 (1)
C(10)	0.0090 (4)	0.0108 (3)	0.0014 (1)	0.0013 (3)	0.0005 (1)	−0.0001 (1)
C(11)	0.0097 (5)	0.0186 (6)	0.0018 (1)	0.0031 (5)	0.0008 (2)	0.0014 (2)
C(12)	0.0087 (6)	0.0146 (6)	0.0038 (2)	0.0001 (5)	0.0001 (2)	0.0040 (2)
C(13)	0.0128 (7)	0.0072 (3)	0.0048 (2)	−0.0029 (4)	−0.0004 (3)	0.0018 (2)
C(14)	0.0116 (5)	0.0053 (2)	0.0028 (1)	−0.0011 (3)	0.0004 (2)	0.0006 (1)
C(15)	0.0182 (6)	0.0042 (2)	0.0020 (1)	−0.0006 (3)	−0.0013 (2)	0.0003 (1)
C(16)	0.0181 (6)	0.0060 (2)	0.0014 (1)	0.0019 (3)	0.0002 (2)	0.0004 (1)
C(17)	0.0117 (4)	0.0071 (3)	0.0018 (1)	0.0021 (3)	−0.0005 (1)	0.0007 (1)
C(18)	0.0163 (5)	0.0032 (2)	0.0014 (1)	0.0009 (3)	0.0007 (2)	−0.0004 (1)
C(19)	0.0115 (4)	0.0049 (2)	0.0015 (1)	−0.0003 (3)	0.0004 (1)	−0.0011 (1)
C(20)	0.0136 (5)	0.0052 (1)	0.0012 (1)	0.0018 (3)	−0.0003 (1)	−0.0006 (1)
C(21)	0.0127 (5)	0.0054 (2)	0.0012 (1)	0.0002 (3)	0.0012 (1)	−0.0004 (1)
C(22)	0.0110 (4)	0.0058 (2)	0.0015 (1)	0.0024 (3)	0.0002 (1)	−0.0008 (1)
C(23)	0.0188 (7)	0.0048 (2)	0.0020 (1)	−0.0042 (3)	−0.0010 (2)	0.0004 (1)
C(24)	0.0129 (5)	0.0084 (3)	0.0017 (1)	−0.0049 (3)	0.0010 (2)	−0.0008 (1)
C(25)	0.0108 (4)	0.0056 (2)	0.0020 (1)	−0.0010 (2)	−0.0010 (2)	−0.0005 (1)
C(26)	0.0136 (5)	0.0060 (2)	0.0012 (1)	−0.0030 (3)	−0.0003 (1)	−0.0006 (1)
C(27)	0.0135 (5)	0.0045 (2)	0.0023 (1)	−0.0006 (3)	−0.0006 (2)	−0.0013 (1)

[a] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$. [b] Isotropic thermal parameters of 5.0 Å^2 were assumed for all hydrogen atoms.

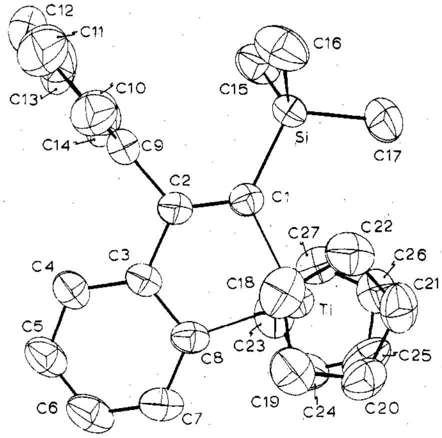


Figure 1. Molecular structure of 1,1-bis(η^5-cyclopentadienyl)-2-trimethylsilyl-3-phenylbenzotitanole with the atoms represented by their 50% probability ellipsoids for thermal motion.

Reaction of Bis(η^5-cyclopentadienyl)diphenyltitanium and Phenyltrimethylsilylacetylene. A mixture of 500 mg (1.5 mmol) of bis(η^5-cyclopentadienyl)diphenyltitanium, 261 mg (1.5 mmol) of phenyltrimethylsilylacetylene, and 10 mL of anhydrous benzene was refluxed for 1.5 h under argon with magnetic stirring. After the addition of alumina, evaporation of the solvent, and chromatography, as described above, elution with 2:1 hexane–benzene removed an orange-red band containing 207 mg (32%) of 1,1-bis(η^5-cyclopentadienyl)-2-trimethylsilyl-3-phenylbenzotitanole (**8**). An analytical sample, mp 201–202 °C, was prepared by recrystallization from ethyl ether–heptane and dried in vacuo at room temperature.

Proton NMR τ (C_6D_6) 10.35 (9 H, s, $Si(CH_3)_3$), 3.05 (10 H, s, η^5-C_5H_5), 2.6–3.1 (ca. 9 H, m, aromatic); IR (KBr) 1237 (m), 1000 (m), 925 (w), 890 (m), 837 (s), 800 (s), 762 (s), 712 (s) cm^{-1}; mass spectrum m/e (%) 428 (95, M^+), 413 (5, $(M - CH_3)^+$), 355 (20, $(M - Si(CH_3)_3)^+$), 254 (90, $(C_{10}H_{10}TiC_6H_4)^+$), 178 (100, $(C_{10}H_{10}Ti)^+$), 113 (55, $(C_5H_5Ti)^+$), 73 (45, $(Si(CH_3)_3)^+$). Anal. Calcd for $C_{27}H_{28}SiTi$: C, 75.67; H, 6.59; Ti, 11.20. Found: C, 75.37; H, 6.73; Ti, 11.50.

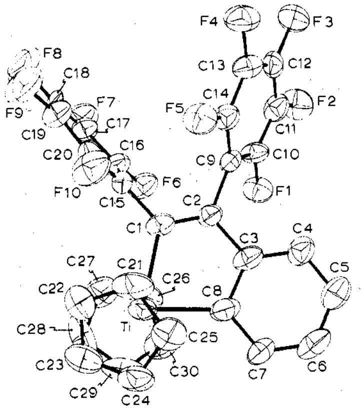


Figure 2. Molecular structure of 1,1-bis(η^5-cyclopentadienyl)-2,3-bis(pentafluorophenyl)benzotitanole.

X-ray Data Collection and Structure Determination for (η^5-$C_5H_5)_2TiC_8H_4(C_6H_5)[Si(CH_3)_3]$. Single crystals of the compound were sealed in thin-walled glass capillaries prior to X-ray examination. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections ($\theta > 20°$) accurately centered on an Enraf-Nonius CAD-4 diffractometer are given in Table I. The space group was uniquely determined from systematic absences in $0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, and $hk0$ for $h = 2n + 1$ to be $Pbca$ [D_{2h}^{15}, No. 61].

Data were collected on the diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω–2θ scan technique with a takeoff angle of 3.0°. The scan rate was variable and was determined by a fast (20° min^{-1}) prescan. Calculated speeds based on the net intensity gathered in the prescan ranged from 7 to 0.4° min^{-1}. Moving-crystal moving-counter backgrounds were collected for 25% of the total scan width at each end of the scan range. For each intensity the scan width was determined by the equation

$$\text{scan range} = A + B \tan \theta$$

where $A = 0.60°$ and $B = 0.20°$. Aperture settings were determined

Table IV. Final Fractional Coordinates for 1,1-Bis(η^5-cyclopentadienyl)-2,3-bis(pentafluorophenyl)benzotitanole

atom	*x/a*	*x/b*	*z/c*
Ti	0.2792 (1)	0.7404 (1)	0.8018 (1)
F(1)	0.3927 (2)	0.6626 (4)	1.1619 (4)
F(2)	0.4567 (2)	0.5518 (4)	1.3058 (4)
F(3)	0.4576 (2)	0.3739 (4)	1.2718 (4)
F(4)	0.3991 (2)	0.3099 (4)	1.0878 (4)
F(5)	0.3391 (2)	0.4219 (4)	0.9413 (4)
F(6)	0.4067 (2)	0.8185 (4)	1.0670 (5)
F(7)	0.5150 (2)	0.8349 (5)	1.1477 (5)
F(8)	0.5744 (4)	0.7190 (5)	1.1020 (5)
F(9)	0.5228 (2)	0.5836 (4)	0.9767 (5)
F(10)	0.4146 (2)	0.5611 (4)	0.8996 (4)
C(1)	0.3442 (3)	0.6734 (6)	0.9334 (7)
C(2)	0.3255 (3)	0.6061 (6)	0.9620 (7)
C(3)	0.2658 (4)	0.5866 (6)	0.9132 (7)
C(4)	0.2426 (4)	0.5222 (6)	0.9446 (8)
C(5)	0.1859 (4)	0.5070 (7)	0.8962 (8)
C(6)	0.1537 (4)	0.5586 (8)	0.8125 (9)
C(7)	0.1765 (4)	0.6238 (8)	0.7808 (9)
C(8)	0.2334 (4)	0.6405 (7)	0.8284 (8)
C(9)	0.3624 (3)	0.5462 (6)	1.0457 (6)
C(10)	0.3933 (4)	0.5760 (6)	1.1392 (7)
C(11)	0.4259 (4)	0.5206 (7)	1.2159 (7)
C(12)	0.4272 (4)	0.4289 (6)	1.1978 (1)
C(13)	0.3966 (4)	0.3972 (6)	1.1058 (8)
C(14)	0.3665 (4)	0.4559 (6)	1.0316 (6)
C(15)	0.4051 (4)	0.6890 (6)	0.9771 (7)
C(16)	0.4333 (4)	0.7588 (7)	1.0436 (7)
C(17)	0.4895 (4)	0.7678 (7)	1.0863 (7)
C(18)	0.5195 (4)	0.7100 (8)	1.0607 (9)
C(19)	0.4934 (4)	0.6401 (7)	0.9975 (8)
C(20)	0.4374 (4)	0.6312 (6)	0.9608 (7)
C(21)	0.2600 (5)	0.8973 (7)	0.7765 (8)
C(22)	0.3052 (4)	0.8869 (6)	0.8687 (8)
C(23)	0.2882 (4)	0.8386 (7)	0.9264 (8)
C(24)	0.2317 (4)	0.8196 (7)	0.8694 (9)
C(25)	0.2148 (4)	0.8562 (7)	0.7745 (8)
C(26)	0.3334 (5)	0.6994 (9)	0.7316 (10)
C(27)	0.3042 (5)	0.6260 (8)	0.7236 (8)
C(28)	0.2494 (5)	0.6437 (9)	0.6645 (9)
C(29)	0.2437 (6)	0.7320 (10)	0.6352 (9)
C(30)	0.2984 (7)	0.7686 (8)	0.6727 (11)
C(31)	−0.0666 (11)	0.5647 (17)	0.0176 (19)
C(32)	−0.0106 (13)	0.5944 (21)	0.1186 (25)
C(33)	−0.0215 (18)	0.6150 (23)	0.2035 (27)
H(1)[C(4)]	0.267	0.484	1.004
H(2)[C(5)]	0.168	0.461	0.921
H(3)[C(6)]	0.113	0.547	0.773
H(4)[C(7)]	0.151	0.661	0.720
H(5)[C(21)]	0.260	0.929	0.720
H(6)[C(22)]	0.344	0.910	0.891
H(7)[C(23)]	0.313	0.820	0.997
H(8)[C(24)]	0.208	0.787	0.892
H(9)[C(25)]	0.176	0.852	0.716
H(10)[C(26)]	0.375	0.705	0.776
H(11)[C(27)]	0.320	0.565	0.756
H(12)[C(28)]	0.218	0.599	0.646
H(13)[C(29)]	0.207	0.765	0.596
H(14)[C(30)]	0.310	0.830	0.658

in a like manner with A = 4 mm and B = 0.87 mm. Other diffractometer parameters and the method of estimation of the standard deviations have been described previously.[18] As a check on the stability of the instrument and crystal, two reflections, (0,0,12) and (020), were measured after every 50 reflections; the standards fluctuated within a range of ±2%.

One independent octant of data was measured out to $2\theta = 50°$, and a slow scan was performed on a total of 2198 unique reflections. Since these data were scanned at a speed which would yield a net count of 4000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 30 was obtained in the prescan. On the basis of these considerations, the data set of 2198 reflections (used in the subsequent structure determination and refinement) was considered observed and consisted in the main of those for which $I > 3\sigma(I)$. The intensities were corrected for Lorentz, polarization, and absorption effects (the estimated minimum and maximum transmission factors were 0.78 and 0.85, respectively).

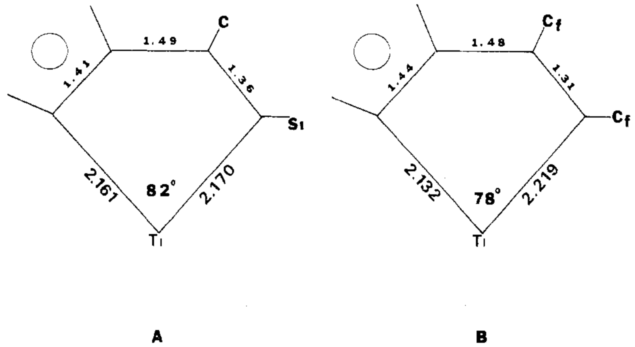


Figure 3. Comparison of some structural parameters of the five-membered heterocyclic rings in $(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6H_5)[Si(CH_3)_3]$ (A) and $(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6F_5)_2$ (B).

Full-matrix, least-squares refinement was carried out using the program ORFLS.[19] The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Atomic scattering factors for Ti, Si, and C were taken from Cromer and Waber;[20] those for H were taken from ref 21.

The position of the titanium atom was deduced by the inspection of a Patterson map, and the subsequent calculation of Fourier maps allowed the locating of the 28 remaining nonhydrogen atoms. Refinement with isotropic temperature factors led to a reliability index of $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.094$. Conversion to anisotropic thermal parameters and further refinement led to $R_1 = 0.049$. The hydrogen atoms of the cyclopentadienyl, phenyl, and indenyl rings were placed at calculated positions 1.00 Å from the bonded carbon atoms and their parameters were not refined. Those of the methyl groups were located on a difference Fourier map and their positional coordinates were varied. Additional cycles of refinement led to final values of $R_1 = 0.032$ and $R_2 = \{\sum(|F_o| - |F_c|)^2/\sum(F_o)^2\}^{1/2} = 0.032$. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. A final difference Fourier map showed no feature greater than 0.3 e/Å^3. The standard deviation of an observation of unit weight was 0.72. Unit weights were used at all stages; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional and thermal parameters are given in Tables II and III.

X-ray Data Collection and Structure Determination for $(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6F_5)_2$. The data collection procedure was identical with that given above except as noted. The space group was determined from systematic absences in hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$ to be Cc or $C2/c$. Subsequent refinement showed the correct choice to be the centric $C2/c$ [C_{2h}, No. 15].

One independent quadrant of data was measured out to $2\theta = 50°$ and a slow scan was performed on a total of 1993 unique reflections. The intensities were corrected for Lorentz and polarization effects but not for absorption, since the estimated minimum and maximum transmission factors were 0.89 and 0.92, respectively. Two standard reflections, (400) and the (020), were measured after every 50 reflections; no significant variation was noted.

Due to the large number of fluorine atoms, the position of the titanium atom could not be deduced from inspection of a Patterson map. However, by use of the direct methods program MULTAN,[22] the positions of the titanium atom and 39 other nonhydrogen atoms were determined. Subsequent calculation of a difference Fourier map afforded the location of the remaining nonhydrogen atoms. Refinement with isotropic temperature factors led to $R_1 = 0.149$. Calculation of a difference Fourier map revealed six diffuse maxima through which a crystallographic twofold axis passed. This was interpreted as a hexane molecule of crystallization and the three independent carbon atoms were included in the refinement. (The isotropic temperature factors of the hexane carbon atoms were so large that it proved necessary to refine only the isotropic values.) The R_1 value was lowered to 0.136. Addition of the hydrogen atoms in calculated positions 1.00 Å from the bonded carbon atoms, conversion of nonhydrogen atoms to anisotropic temperature factors, and further refinement gave final R values of $R_1 = 0.070$ and $R_2 = 0.078$. The largest parameter shifts in the final cycle of refinement were less than 0.10 of their estimated standard deviations. A final difference Fourier map showed several

Table V. Thermal Parameters[a,b] for 1,1-Bis(η^5-cyclopentadienyl)-2,3-bis(pentafluorophenyl)benzotitanole

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ti	0.00143 (2)	0.00363 (10)	0.00488 (11)	0.00060 (5)	0.00064 (5)	0.00033 (10)
F(1)	0.0023 (1)	0.0043 (4)	0.0052 (4)	−0.0002 (2)	0.0012 (2)	−0.0013 (3)
F(2)	0.0024 (1)	0.0071 (4)	0.0036 (4)	−0.0006 (2)	0.0004 (2)	−0.0005 (3)
F(3)	0.0020 (1)	0.0064 (4)	0.0066 (4)	0.0008 (2)	0.0010 (2)	0.0027 (3)
F(4)	0.0030 (2)	0.0035 (4)	0.0083 (5)	0.0007 (2)	0.0020 (2)	0.0000 (3)
F(5)	0.0023 (1)	0.0046 (3)	0.0048 (4)	0.0001 (2)	0.0011 (2)	−0.0008 (3)
F(6)	0.0021 (1)	0.0048 (4)	0.0094 (5)	−0.0001 (2)	0.0010 (2)	−0.0022 (4)
F(7)	0.0024 (2)	0.0077 (5)	0.0100 (6)	−0.0015 (2)	0.0007 (2)	−0.0028 (4)
F(8)	0.0011 (1)	0.0103 (5)	0.0156 (6)	−0.0009 (2)	0.0010 (2)	0.0009 (5)
F(9)	0.0014 (1)	0.0085 (4)	0.0095 (5)	0.0010 (2)	0.0018 (2)	0.0009 (4)
F(10)	0.0015 (1)	0.0049 (3)	0.0079 (5)	0.0005 (2)	0.0011 (2)	−0.0008 (3)
C(1)	0.0011 (2)	0.0034 (5)	0.0051 (6)	0.0006 (2)	0.0007 (3)	−0.0005 (5)
C(2)	0.0011 (2)	0.0026 (5)	0.0056 (7)	0.0000 (2)	0.0005 (3)	0.0003 (4)
C(3)	0.0012 (2)	0.0038 (6)	0.0060 (7)	0.0000 (3)	0.0006 (3)	−0.0010 (5)
C(4)	0.0016 (2)	0.0039 (6)	0.0073 (8)	−0.0004 (3)	0.0014 (3)	−0.0002 (6)
C(5)	0.0017 (2)	0.0053 (7)	0.0086 (9)	−0.0002 (3)	0.0023 (4)	−0.0014 (6)
C(6)	0.0012 (2)	0.0080 (9)	0.0095 (10)	−0.0006 (4)	0.0011 (4)	−0.0011 (8)
C(7)	0.0011 (2)	0.0064 (8)	0.0092 (10)	−0.0003 (3)	0.0010 (4)	0.0013 (7)
C(8)	0.0012 (2)	0.0054 (6)	0.0065 (8)	0.0001 (3)	0.0004 (3)	0.0006 (6)
C(9)	0.0009 (2)	0.0034 (6)	0.0044 (6)	−0.0002 (2)	0.0007 (3)	0.0002 (4)
C(10)	0.0014 (2)	0.0036 (6)	0.0048 (6)	−0.0001 (3)	0.0011 (3)	−0.0003 (5)
C(11)	0.0015 (2)	0.0058 (7)	0.0039 (6)	−0.0003 (3)	0.0004 (3)	−0.0004 (5)
C(12)	0.0012 (2)	0.0045 (7)	0.0060 (7)	0.0002 (3)	0.0016 (3)	0.0016 (6)
C(13)	0.0016 (2)	0.0035 (6)	0.0067 (8)	−0.0003 (3)	0.0014 (4)	−0.0006 (6)
C(14)	0.0014 (2)	0.0036 (6)	0.0040 (6)	0.0000 (3)	0.0003 (3)	−0.0006 (5)
C(15)	0.0012 (2)	0.0039 (6)	0.0050 (6)	−0.0003 (3)	0.0008 (3)	0.0011 (5)
C(16)	0.0018 (2)	0.0043 (6)	0.0056 (6)	−0.0000 (3)	0.0019 (3)	0.0005 (5)
C(17)	0.0018 (2)	0.0064 (8)	0.0052 (7)	−0.0011 (3)	0.0006 (3)	−0.0007 (6)
C(18)	0.0009 (2)	0.0007 (8)	0.0090 (10)	−0.0002 (3)	0.0005 (4)	0.0007 (7)
C(19)	0.0011 (2)	0.0053 (7)	0.0061 (3)	0.0006 (3)	0.0011 (3)	0.0010 (6)
C(20)	0.0011 (2)	0.0044 (6)	0.0058 (7)	0.0002 (3)	0.0006 (3)	0.0003 (5)
C(21)	0.0026 (3)	0.0050 (7)	0.0058 (8)	0.0014 (4)	0.0017 (4)	0.0004 (6)
C(22)	0.0027 (3)	0.0034 (6)	0.0065 (8)	0.0002 (3)	0.0025 (4)	−0.0006 (5)
C(23)	0.0022 (3)	0.0033 (6)	0.0081 (9)	0.0012 (3)	0.0001 (4)	−0.0004 (6)
C(24)	0.0020 (3)	0.0041 (6)	0.0095 (10)	0.0010 (3)	0.0022 (4)	0.0002 (6)
C(25)	0.0018 (3)	0.0046 (7)	0.0076 (9)	0.0013 (3)	0.0010 (4)	0.0008 (6)
C(26)	0.0021 (3)	0.0075 (10)	0.0105 (12)	0.0008 (4)	0.0022 (5)	−0.0005 (9)
C(27)	0.0029 (3)	0.0050 (8)	0.0073 (9)	0.0011 (4)	0.0020 (5)	0.0000 (7)
C(28)	0.0025 (3)	0.0077 (10)	0.0089 (10)	−0.0006 (4)	0.0013 (5)	−0.0019 (8)
C(29)	0.0034 (4)	0.0091 (12)	0.0071 (9)	0.0026 (6)	0.0002 (5)	0.0012 (8)
C(30)	0.0060 (6)	0.0048 (9)	0.0124 (14)	−0.0007 (6)	0.0055 (8)	0.0016 (9)
C(31)	$B = 17.6$ (8) Å^2					
C(32)	$B = 21.4$ (1.1) Å^2					
C(33)	$B = 28.4$ (1.6) Å^2					

[a] Anisotropic thermal parameters are as defined in Table III. [b] Isotropic thermal parameters of 6.0 Å^2 were assumed for all hydrogen atoms.

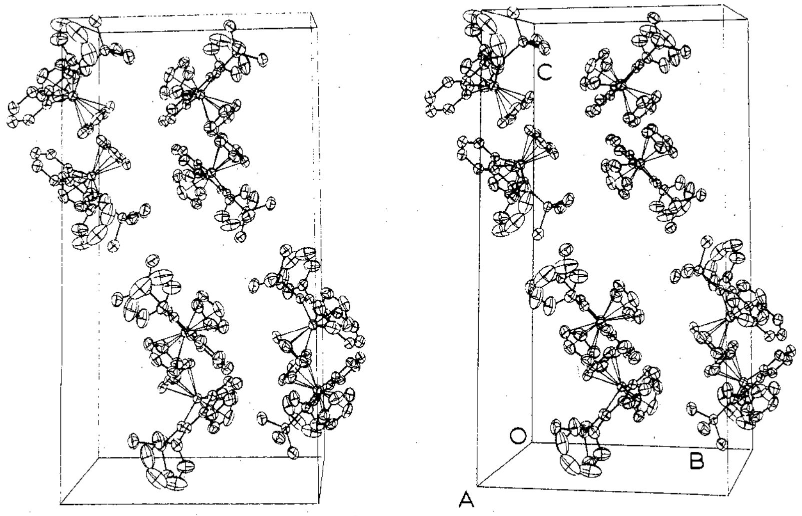


Figure 4. Stereoscopic view of the unit cell packing of 1,1-bis(η^5-cyclopentadienyl)-2-trimethylsilyl-3-phenylbenzotitanole.

peaks of ~0.6 e/Å^3, but they were in the vicinity of the fluorine atoms. The standard deviation of an observation of unit weight was 1.26. Unit weights were used and no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional and thermal parameters are given in Tables IV and V.

Results and Discussion

Hagihara and co-workers[5] have previously shown that a thermal reaction between $(\eta^5\text{-}C_5H_5)_2TiPh_2$ and diphenylacetylene produces in moderate yield an organometallic

Table VI. Interatomic Distances (Å) and Angles (deg) for 1,1-Bis(η^5-cyclopentadienyl)-2-trimethylsilyl-3-phenylbenzotitanole

Bond Distances			
Ti-C(1)	2.170 (3)	Ti-C(8)	2.161 (3)
Ti-C(18)	2.386 (3)	Ti-C(23)	2.370 (4)
Ti-C(19)	2.398 (4)	Ti-C(24)	2.381 (4)
Ti-C(20)	2.403 (4)	Ti-C(25)	2.371 (4)
Ti-C(21)	2.379 (3)	Ti-C(26)	2.374 (4)
Ti-C(22)	2.360 (4)	Ti-C(27)	2.367 (4)
Av Ti-C(π) = 2.379			
Ti-cent(1)	2.069	Ti-cent(2)	2.057
C(1)-C(2)	1.364 (4)	C(5)-C(6)	1.370 (5)
C(2)-C(3)	1.486 (4)	C(6)-C(7)	1.389 (5)
C(3)-C(4)	1.405 (4)	C(7)-C(8)	1.399 (4)
C(4)-C(5)	1.387 (5)	C(8)-C(3)	1.409 (4)
C(2)-C(9)	1.502 (4)	C(9)-C(10)	1.384 (5)
C(10)-C(11)	1.384 (6)	C(11)-C(12)	1.333 (9)
C(12)-C(13)	1.369 (9)	C(13)-C(14)	1.394 (7)
C(14)-C(9)	1.359 (5)	C(1)-Si	1.878 (3)
Si-C(15)	1.868 (4)	Si-C(16)	1.870 (4)
Si-C(17)	1.865 (4)	C(18)-C(19)	1.389 (5)
C(19)-C(20)	1.390 (5)	C(20)-C(21)	1.393 (5)
C(21)-C(22)	1.407 (5)	C(22)-C(18)	1.398 (5)
C(23)-C(24)	1.370 (6)	C(24)-C(25)	1.410 (6)
C(25)-C(26)	1.404 (5)	C(26)-C(27)	1.383 (5)
C(27)-C(23)	1.385 (6)		
Bond Angles			
C(1)-Ti-cent(2)	108.8	C(8)-Ti-cent(1)	105.8
C(1)-Ti-cent(1)	106.2	C(8)-Ti-cent(2)	103.7
C(1)-Ti-C(8)	81.8 (1)	cent(1)-Ti-cent(2)	136.7
Si-C(1)-Ti	127.4 (2)	C(4)-C(3)-C(8)	120.4 (3)
Si-C(1)-C(2)	123.0 (2)	C(3)-C(4)-C(5)	120.0 (3)
C(2)-C(1)-Ti	109.6 (2)	C(4)-C(5)-C(6)	120.2 (4)
C(1)-C(2)-C(3)	120.9 (3)	C(5)-C(6)-C(7)	120.2 (3)
C(1)-C(2)-C(9)	116.0 (3)	C(6)-C(7)-C(8)	121.6 (3)
C(9)-C(2)-C(3)	123.0 (3)	C(7)-C(8)-Ti	132.1 (3)
C(2)-C(3)-C(4)	122.2 (3)	C(7)-C(8)-C(3)	117.6 (3)
C(2)-C(3)-C(8)	117.3 (3)	C(3)-C(8)-Ti	110.2 (3)
C(1)-Si-C(15)	112.1 (2)	C(15)-Si-C(16)	109.2 (2)
C(1)-Si-C(16)	113.1 (2)	C(16)-Si-C(17)	104.2 (2)
C(1)-Si-C(17)	111.6 (2)	C(17)-Si-C(15)	106.1 (2)
C(2)-C(9)-C(10)	121.1 (3)	C(10)-C(11)-C(12)	120.3 (6)
C(2)-C(9)-C(14)	120.7 (3)	C(11)-C(12)-C(13)	121.1 (6)
C(10)-C(9)-C(14)	118.2 (4)	C(12)-C(13)-C(14)	118.6 (6)
C(9)-C(10)-C(11)	120.4 (5)	C(13)-C(14)-C(9)	121.4 (5)
C(18)-C(19)-C(20)	108.3 (4)	C(23)-C(24)-C(25)	108.0 (4)
C(19)-C(20)-C(21)	108.2 (4)	C(24)-C(25)-C(26)	108.8 (4)
C(20)-C(21)-C(22)	107.7 (4)	C(25)-C(26)-C(27)	108.3 (4)
C(21)-C(22)-C(18)	107.6 (3)	C(26)-C(27)-C(23)	107.8 (4)
C(22)-C(18)-C(19)	108.1 (3)	C(17)-C(23)-C(24)	107.0 (4)

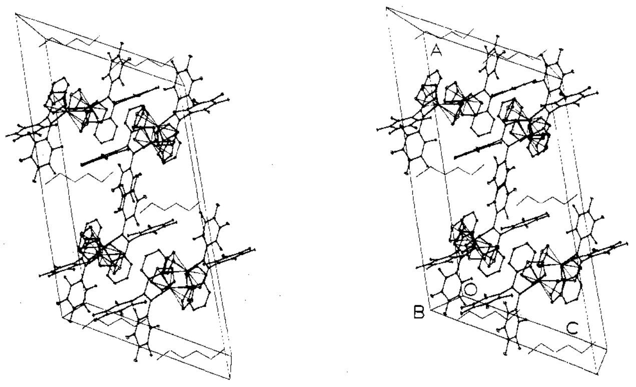


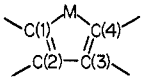
Figure 5. Stereoscopic view of the unit cell packing of 1,1-bis(η^5-cyclopentadienyl)-2,3-bis(pentafluorophenyl)benzotitanole. The atoms of the organometallic moiety are represented by their 20% ellipsoids, and the hexane molecules of crystallization are shown as connected lines.

Table VII. Intramolecular Distances (Å) and Angles (deg) for 1,1-Bis(η^5-cyclopentadienyl)-2,3-bis(pentafluorophenyl)-benzotitanole

Bond Distances			
Ti-C(1)	2.219 (9)	Ti-C(8)	2.132 (10)
Ti-C(21)	2.388 (10)	Ti-C(26)	2.345 (13)
Ti-C(22)	2.379 (10)	Ti-C(27)	2.396 (11)
Ti-C(23)	2.361 (11)	Ti-C(28)	2.390 (12)
Ti-C(24)	2.376 (11)	Ti-C(29)	2.316 (13)
Ti-C(25)	2.372 (10)	Ti-C(30)	2.377 (14)
Ti-cent(1)	2.054	Ti-cent(2)	2.051
C(1)-C(2)	1.31 (1)	C(5)-C(6)	1.41 (1)
C(2)-C(3)	1.48 (1)	C(6)-C(7)	1.38 (2)
C(3)-C(4)	1.37 (1)	C(7)-C(8)	1.41 (1)
C(4)-C(5)	1.40 (1)	C(8)-C(3)	1.44 (1)
C(1)-C(15)	1.51 (1)	C(2)-C(9)	1.51 (1)
C(15)-C(16)	1.41 (1)	C(9)-C(10)	1.37 (1)
C(16)-C(17)	1.38 (1)	C(10)-C(11)	1.38 (1)
C(17)-C(18)	1.39 (1)	C(11)-C(12)	1.40 (1)
C(18)-C(19)	1.38 (1)	C(12)-C(13)	1.36 (1)
C(19)-C(20)	1.38 (1)	C(13)-C(14)	1.37 (1)
C(20)-C(15)	1.36 (1)	C(14)-C(9)	1.38 (1)
F(5)-C(16)	1.32 (1)	F(1)-C(10)	1.34 (1)
F(7)-C(17)	1.33 (1)	F(2)-C(11)	1.33 (1)
F(8)-C(18)	1.35 (1)	F(3)-C(12)	1.34 (1)
F(9)-C(19)	1.32 (1)	F(4)-C(13)	1.34 (1)
F(10)-C(20)	1.35 (1)	F(5)-C(14)	1.34 (1)
C(21)-C(22)	1.39 (1)	C(26)-C(27)	1.33 (2)
C(22)-C(23)	1.41 (2)	C(27)-C(28)	1.37 (2)
C(23)-C(24)	1.41 (1)	C(28)-C(29)	1.38 (2)
C(24)-C(25)	1.44 (2)	C(29)-C(30)	1.44 (2)
C(25)-C(21)	1.39 (2)	C(30)-C(26)	1.41 (2)
C(31)-C(32)	1.66 (3)	C(32)-C(33)	1.54 (5)
Bond Angles			
C(1)-Ti-cent(2)	107.2	C(8)-Ti-cent(1)	105.5
C(1)-Ti-cent(1)	108.3	C(8)-Ti-cent(2)	105.3
C(1)-Ti-C(8)	78.3 (4)	cent(1)-Ti-cent(2)	136.7
C(15)-C(1)-C(2)	120.6 (8)	C(8)-C(3)-C(4)	122.0 (9)
C(1)-C(2)-C(3)	120.4 (8)	C(3)-C(4)-C(5)	121.3 (1.0)
C(1)-C(2)-C(9)	122.6 (8)	C(4)-C(5)-C(6)	117.3 (1.0)
C(9)-C(2)-C(3)	117.1 (8)	C(5)-C(6)-C(7)	121.8 (9)
C(2)-C(1)-Ti	112.7 (7)	C(3)-C(8)-Ti	114.0 (7)
C(15)-C(1)-Ti	125.7 (7)	C(7)-C(8)-Ti	130.2 (7)
C(2)-C(3)-C(4)	123.6 (9)	C(6)-C(7)-C(8)	121.8 (1.0)
C(2)-C(3)-C(8)	114.3 (9)	C(7)-C(8)-C(3)	115.7 (1.0)
C(1)-C(15)-C(16)	123.3 (9)	C(2)-C(9)-C(10)	123.6 (8)
C(1)-C(15)-C(20)	121.2 (8)	C(2)-C(9)-C(14)	120.8 (8)
C(20)-C(15)-C(16)	115.2 (8)	C(10)-C(9)-C(14)	115.6 (8)
C(15)-C(16)-C(17)	121.7 (9)	C(9)-C(10)-C(11)	123.4 (9)
C(15)-C(16)-F(6)	121.2 (8)	C(9)-C(10)-F(1)	121.0 (8)
F(6)-C(16)-C(17)	117.3 (9)	F(1)-C(10)-C(11)	115.6 (8)
C(16)-C(17)-C(18)	120.0 (9)	C(10)-C(11)-C(12)	118.5 (9)
C(16)-C(17)-F(7)	120.5 (1.0)	C(10)-C(11)-F(2)	122.2 (9)
F(7)-C(17)-C(18)	119.4 (9)	F(2)-C(11)-C(12)	119.3 (9)
C(17)-C(18)-C(19)	119.7 (9)	C(11)-C(12)-C(13)	119.4 (9)
C(17)-C(18)-F(8)	120.0 (1.0)	C(11)-C(12)-F(3)	119.3 (9)
F(8)-C(18)-C(19)	120.1 (1.0)	F(3)-C(12)-C(13)	121.3 (9)
C(18)-C(19)-C(20)	117.8 (1.0)	C(12)-C(13)-C(14)	119.6 (9)
C(18)-C(19)-F(9)	119.1 (8)	C(12)-C(13)-F(4)	119.4 (9)
F(9)-C(19)-C(20)	123.0 (9)	F(4)-C(13)-C(14)	120.8 (9)
C(19)-C(20)-C(16)	125.3 (9)	C(13)-C(14)-C(9)	123.3 (8)
C(19)-C(20)-F(10)	114.6 (9)	C(13)-C(14)-F(5)	117.3 (8)
F(10)-C(20)-C(16)	120.0 (8)	F(5)-C(14)-C(9)	119.4 (8)
C(21)-C(22)-C(23)	108.2 (1.0)	C(26)-C(27)-C(28)	109.5 (1.0)
C(22)-C(23)-C(24)	108.2 (1.0)	C(27)-C(28)-C(29)	108.6 (1.2)
C(23)-C(24)-C(25)	106.6 (1.0)	C(28)-C(29)-C(30)	107.3 (1.1)
C(24)-C(25)-C(21)	108.0 (9)	C(29)-C(30)-C(26)	104.3 (1.0)
C(25)-C(21)-C(22)	109.0 (1.0)	C(30)-C(26)-C(27)	109.9 (1.1)
C(31)-C(32)-C(33)	113.4 (2.8)	C(33)′-C(33)-C(32)	119.3 (5.9)

product which on the basis of chemical and spectral data was formulated as a titanaindene derivative (**6**). This process was later postulated to proceed by insertion of the acetylene into the carbon–titanium σ bond of an intermediate $(C_5H_5)_2Ti(C_6H_4)$ species.[23] Subsequent investigations in our laboratory have shown that a variety of symmetrical and unsymmetrical acetylenes undergo this novel reaction and that

Table VIII. Comparison of Structural Parameters of Metallocyclic Rings[a]



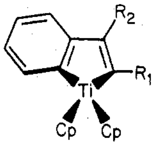
compd	M-C(1), Å	M-C(4), Å	C(1)-M-C(4), deg	C(1)-C(2), Å	C(2)-C(3), Å	C(3)-C(4), Å	Δ of M from plane of C(1) → C(4), Å	ref
$(\eta^5\text{-}C_5H_5)[P(C_6H_5)_3]CoC_4(C_6F_5)_4$	1.995 (11)	1.993 (11)	82.4 (4)	1.326 (15)	1.467 (16)	1.335 (15)	0.203	3
$(\eta^5\text{-}C_5H_5)[P(C_6H_5)_3]RhC_4(C_6F_5)_4$	2.067 (11)	2.060 (12)	78.3 (4)	1.354 (15)	1.457 (16)	1.343 (16)	0.239	4
$[Sb(C_6H_5)_3]ClRhC_4(CF_3)_4\cdot CH_2Cl_2$	2.000 (10)	1.964 (11)	77.2 (4)	1.330 (16)	1.388 (14)	1.367 (15)	0.001	[b]
$[As(CH_3)_3]Cl(H_2O)RhC_4(CF_3)_4$	2.047 (16)	1.998 (16)	80.2 (6)	1.311 (24)	1.433 (26)	1.346 (23)	0.001	[c]
$(\eta^5\text{-}C_5H_5)_2HfC_4(C_6H_5)_4$	2.22 (2)	2.18 (2)	78.7 (8)	1.39 (3)	1.51 (3)	1.36 (2)	0.040	2
$(\eta^5\text{-}C_5H_5)_2TiC_4(C_6H_5)_4$	2.172 (5)	2.141 (5)	80.3 (2)	1.369 (6)	1.495 (6)	1.370 (6)	0.030	2
$(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6F_5)_2$	2.219 (9)	2.132 (10)	78.3 (4)	1.31 (1)	1.48 (1)	1.44 (1)		this study
$(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6H_5)[Si(CH_3)_3]$	2.170 (3)	2.161 (3)	81.8 (1)	1.364 (4)	1.486 (4)	1.409 (4)		this study

[a] C(1) is associated with the longer of the two Ti-C(σ) bond lengths. C(4) is C(8) in the titanaindenes. [b] J. T. Mague, *Inorg. Chem.*, 9, 1610 (1970). [c] J. T. Mague, *ibid.*, 12, 2649 (1973).

Table IX. Summary of Ti-C (σ) Bond Lengths

compd	Ti electronic confign	C hybridizn	length, Å	ref
$Cp_2TiC_4Ph_4$	d^0	sp^2	2.172 (5) 2.156 (22) 2.141 (5)	2
$Cp_2Ti(PhCOO)$	d^0	sp^2	2.20	25
$[Cp_2(CF_3C{=}CHCF_3)Ti]_2O$	d^0	sp^2	2.27	25
Cp_2TiPh_2	d^0	sp^2	2.272 (14)	27
$[(PhCH_2)_3Ti]_2O$	d^0	sp^3	2.08 (1)	28
$(PhCH_2)_4Ti$	d^0	sp^3	2.14 (4)[b]	29
			2.13 (4)[c]	30
IND_2TiMe_2[a]	d^0	sp^3	2.21 (2)	31
Cp_2TiCp_2	d^0	sp^3	2.332 (2)	32
$Cp_2Ti(C_6H_3Me_2)$	d^1	sp^2	2.178 (7)	33
$CpTi(OC_6H_4CH_2NMe_2)_2$	d^1	sp^2	2.197 (6)	34

[a] IND represents the indenyl group. [b] Room temperature. [c] −40 °C.



6, R_1, R_2 = Ph
7, R_1, R_2 = C_6F_5
8, R_1 = $SiMe_3$, R_2 = Ph
9, R_1 = Ph, R_2 = $SiMe_3$

the method indeed represents a general route to substituted titanaindenes of this type.

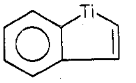
In the present study, reactions of $(\eta^5\text{-}C_5H_5)_2TiPh_2$ with two such acetylenes, $C_6F_5C{\equiv}CC_6F_5$ and $C_6H_5C{\equiv}CSiMe_3$, are described. In each instance, orange-red crystalline products were obtained whose compositions and spectral properties (see Experimental Section) were consistent with the titanaindene structures **7** and **8**, respectively. It was not immediately obvious, however, whether the single product obtained from reaction of the unsymmetrical acetylene was actually **8** or its isomer **9**. In view of this uncertainty and also in view of the lack of *any* structural data on uncoordinated metalloindenes (main group or transition metals), single-crystal X-ray crystallographic investigations of both products were undertaken.

The molecular structures of 1,1-bis(η^5-cyclopentadienyl)-2-trimethylsilyl-3-phenylbenzotitanole and 1,1-bis(η^5-cyclopentadienyl)-2,3-bis(pentafluorophenyl)benzotitanole are shown in Figures 1 and 2, respectively, while the important bond lengths and angles are listed in Tables VI and VII. For clarity of comparison, the parameters of five-membered metallocyclic ring systems which contain a single metal atom are given in Table VIII, and the two titanaindenes are further illustrated in Figure 3. A survey of the data on metallocyclopentadienes affords three major conclusions. (1) The π-electron density is localized between C(1)–C(2) and C(3)–C(4). This is especially apparent in the well-determined structure of $(\eta^5\text{-}C_5H_5)_2TiC_4(C_6H_5)_4$ but is also borne out by the averages for the other six determinations: C(1)–C(2) = 1.35 Å, C(2)–C(3) = 1.46 Å, C(3)–C(4) = 1.35 Å. (2) There is no chemically important difference between the two metal–carbon σ bonds. In some cases the two lengths are significantly different from a mathematical standpoint, but there is no evidence that this is more than a crystallographic artifact. (3) The metal–carbon σ bond lengths are normal with respect to those found in other molecules which present an equivalent hybridization situation.

Although the metalloindenes also exhibit a five-membered heterocyclic ring system, the presence of the aromatic ring fused to two of the carbon atoms causes important differences. The C(1)–C(2) bond lengths are substantially shorter than those of C(3)–C(8): 1.31 (1) vs. 1.44 (1) Å for $(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6F_5)_2$ and 1.364 (4) vs. 1.409 (4) Å for $(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6H_5)[Si(CH_3)_3]$. This is in accordance with the idea of a full double bond between C(1) and C(2) but only a delocalized double bond of an aromatic nature involving C(3) and C(8). As is shown in Figure 3, there is no localization of the π-electron density in the six-membered ring. It may also be noted that the C(2)–C(3) bond lengths appear as normal σ bonds between two sp^2 hybridized carbon atoms. The bonding in the metalloindene may, therefore, be best represented as in **10**.

The pattern of bond distances for the carbon skeleton of the metalloindenes is similar to that found for styrene-type molecules (**11**). This point may be illustrated by reference to the structure of the cinnamic acid family, with the bond lengths found in β-chloro-*cis*-cinnamic acid[24] given in **12**. The apparent effect of the titanium atom on the bond lengths within the C_8 framework is very small.

In $(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6H_5)[Si(CH_3)_3]$, the two Ti–C (σ) bond lengths, 2.161 (3) and 2.170 (3) Å, are nearly equal (Δ = 2.1σ), but with $(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6F_5)_2$ they are quite different, 2.132 (10) and 2.219 (9) Å (Δ = 6.7σ). There appears to be no persuasive electronic explanation for this observation, but the result is easily interpreted in terms of steric effects. The interactions between the cyclopentadienyl groups and the ligand bonded to C(1) are important for the specification of the Ti–C(1) bond lengths. With the more bulky C_6F_5 ligands, this bond is weakened. Support for the idea is found in the closest carbon (cyclopentadienyl) ligand approach, 2.96 Å for the C_6F_5 case compared with 3.56 Å for that of $Si(CH_3)_3$, while the Ti–C(1)–X angles, 125.7° for X = C and



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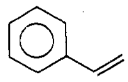

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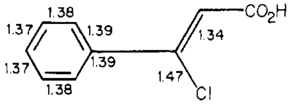

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127.5° for X = Si, are essentially the same. In $(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6F_5)_2$ the Ti–C(1) bond at 2.219 (9) Å is longer than might be expected and the Ti–C(8) bond is shorter at 2.132 (10) Å. The average, 2.176 (61) Å, is, however, comparable to that found for $(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6H_5)[Si(CH_3)_3]$, 2.166 (6) Å, and for $(\eta^5\text{-}C_5H_5)_2TiC_4(C_6H_5)_4$, 2.156 (22) Å.

A tabulation of titanium–carbon σ bond lengths is given in Table IX. Even though ten structures are now available, more must be determined before clear-cut trends emerge. The values from the titanaindene structures are internally consistent and the average of 2.17 Å falls in the middle of the range shown in Table IX.

The average Ti–C(η^5) bond length in $(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6F_5)_2$ is 2.370 (23) Å, and the Ti-ring centroid distance is 2.049 Å. The related values for $(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6H_5)[Si(CH_3)_3]$ are 2.379 (13) and 2.052 Å. In both cases the averages compare favorably with those found for other Ti^{4+} cyclopentadienyl complexes.

The accuracy of the refinement of the structure of $(\eta^5\text{-}C_5H_5)_2TiC_8H_4(C_6F_5)_2$ was marred by the presence of an ill-defined hexane molecule positioned about a crystallographic twofold axis. The guest molecules either were disordered or exhibited extremely high thermal motion. The isotropic temperature factors for the three independent carbon atoms ranged from 24 to 30 Å^2, and it was not possible to refine them anisotropically. Nevertheless, the C–C bond lengths (1.54 (5), 1.58 (4), 1.66 (3) Å) and C–C–C bond angles (113 (3), 119(6)°) are quite reasonable for a hexane molecule. In the related perfluorophenyl compounds $(\eta^5\text{-}C_5H_5)[P(C_6H_5)_3]CoC_4(C_6F_5)_4$ and $(\eta^5\text{-}C_5H_5)[P(C_6H_5)_3]RhC_4(C_6F_5)_4$, a similar problem was encountered, but it was not even possible to locate the atoms or specifically identify the guest.

The unit cell packing for the titanaindenes, shown in Figures 4 and 5, is typical of molecular compounds of this type.

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Registry No. **7**, 67577-11-1; **8**, 67577-12-2; $(\eta^5\text{-}C_5H_5)_2TiPh_2$, 1273-09-2; $C_6F_5C{\equiv}CC_6F_5$, 13557-43-2; $C_6H_5C{\equiv}CSiMe_3$, 2170-06-1.

Supplementary Material Available: A listing of structure factor amplitudes for both structures (27 pages). Ordering information is given on any current masthead page.

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