sufficient to compensate for the destabilization of the π bond that accompanies the decrease of the internuclear distance. The multiple bond may be destabilized by reduced π acidity of the ligand or by steric interaction between the ligand and the metal fragment, which would be manifest as an additional potential energy curve not shown in Figure 9. If the multiple-bond minimum rises above the σ-bond minimum, then the ligand "jumps" to the outer minimum. In this model, it is possible that a ligand might be sterically destabilized when multiply bonded and not sterically destabilized when it serves as a pure σ donor in the same complex.

With this model in mind, it is understandable why incipient phosphorus(III) ligands behave only as σ donors in the transition states of entering-ligand-dependent substitution reactions. In this case, the M–P bond in the transition state is expected to be quite long and would only possess σ-bond character. $L_2Mo(CO)_4$ and $L_3Mo(CO)_3$ are families of relatively crowded complexes even for σ-donor ligands. Such steric congestion appears to prevent potential π-acid ligands ($P(OMe)_3$ and $P(OPh)_3$) from approaching close enough to form a Mo–P p bond. Accordingly, these potential π acids reside in the less sterically demanding σ-bond positions.

The idea that the potential energy curve for the M–P bond is described by a double potential energy minimum suggests that these compounds are related to the extremely rare class of compounds called bond stretch isomers. These isomers exist in two isomeric forms that differ only in the length of one or more bonds.[38] If our model of the M–P bond is correct, then bond stretch isomerism will be found to be more widespread in organometallic and inorganic chemistry than is now observed.

Conclusion

From the results described herein, we conclude that in the absence of π-bonding and steric effects the length of the M–P σ bond is virtually constant. These σ-donor ligands include the trialkylphosphines, mixed alkylarylphosphines, and triarylphosphines, $P(CH_2CH_2CN)_3$, PPh_xH_{3-x}, and PPh_xCl_{3-x} for (η-Cp)(CO)(L)FeCOMe and $LNi(CO)_3$. The Fe–P bonds are significantly shorter for those ligands possessing P–O bonds. We find that the results of the QALE analyses presented herein and elsewhere[1-7] are compelling evidence for the existence of steric thresholds that are sharp enough to allow the use of a switching function to describe the onset of these effects.

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A Stable Titanacyclo-2-pentene: Synthesis and Structure of 3,3-Bis(η^5-cyclopentadienyl)-4,5-diphenyl-3-titanatetracyclo[5.5.1.0^{2,6}.0^{8,12}]trideca-4,8,11-triene

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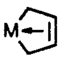
The title compound was synthesized by the reduction of Cp_2TiCl_2 with Mg in the presence of tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene and diphenylacetylene. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 8.447$ (2) Å, $b = 18.389$ (4) Å, $c = 19.210$ (4) Å, and $V = 2984$ (1) Å.^{3} The final agreement for all data was $R(F) = 5.73\%$. ^{1}H and ^{13}C NMR spectral assignments are made with the aid of 2D-COSY and HETCOR NMR studies.

Introduction

A relatively large number of group 4 metallacyclo-3-pentenes have been reported; most of these are zirconocene and hafnocene derivatives,[1-5] although a few titanocene derivatives are known.[5] These complexes are related to metallacycles of conjugated cis dienes, and their general structures are illustrated by structure A. The synthesis and chemistry of these metallacyclo-3-pentenes have been reviewed.[6,7]



A

B

Metallacyclo-2-pentenes arise from cyclization reactions of a reduced metal center with an alkyne and alkene. The general structure of these species is shown by B.

Numerous examples of group 4 metallacyclo-2-pentenes are known, particularly zirconaindans, which are prepared from the stepwise cyclization reactions of (η^2-dehydrobenzene)dicyclopentadienylzirconium with various alkenes. Analogous metallacyclo-2-pentenes from cyclohexyne and

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† X-ray structure determination.

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alkenes are also known. This area has been reviewed recently.[8]

At least three solid-state structures have been reported for metallacyclo-2-pentene compounds. One of these is the cobalt compound $Cp(PPh_3)(\overline{CoCR^1{=}CR^2CHR^3CHR^4})$ ($R = Ph$, $R^2 = R^3 = R^4 = CO_2CH_3$), synthesized from the stepwise cyclization of the cobalt center with methyl phenylpropiolate and dimethyl fumarate.[9] A nickel compound, $(Me_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$, has also been reported recently, which was shown to possess the nickelaindan structure,[10] and 1,1-dicyclopentadienyl-2,3-diphenyl-1-hafnacyclo-2-pentene has also been structurally determined;[11] to the best of our knowledge, this is the only group 4 metallacyclo-2-pentene whose crystal structure has been reported to date.

We have recently investigated the syntheses of η^5-tricyclo[5.2.1.0^{2,6}]deca-2,5,8-trienyl compounds of iron and the group 4 metals in order to prepare η^5-cyclopentadienyl compounds containing a polymerizable group on the cyclopentadienyl ring.[12,13] Further investigation of the chemistry of the triene has led to the cyclization of the 8,9-double bond of the triene with diphenylacetylene and "Cp_2Ti" to produce a titanacyclo-2-pentene compound, which is the subject of this work.

Experimental Section

Starting Materials and Solvents. Neutral alumina (Brockmann I, standard grade, 150 mesh) was purchased from Aldrich, heated in an oven at 110 °C, mixed with heating on a rotary evaporator under high vacuum, deactivated with argon-saturated water (5% by weight), and stored under argon until used. Hexane and pentane (reagent, Fisher) were refluxed over lithium aluminum hydride and distilled under nitrogen before used. Magnesium powder (Fisher, 70–80 mesh) was used as received. Tetrahydrofuran and benzene (Fisher, reagent) were refluxed over sodium/benzophenone and distilled under nitrogen immediately before use. Titanocene dichloride and diphenylacetylene were purchased from Aldrich and used as received.

Tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene was synthesized according to literature methods[14] and characterized by elemental analysis (Midwest Microlab, Indianapolis, IN) and NMR spectrometry.

Physical Methods. NMR spectra (^1H, ^{13}C, 2D-COSY, and HETCOR) were obtained on a Varian (VXR) 300-MHz spectrometer. Two-dimensional homonuclear correlation spectra (2D-COSY)[15] were obtained with phase-sensitive detection according to the method of States et al.[16] 2D NMR symmetrization techniques were not used for any of the spectra collected. Two-dimensional heteronuclear shift-correlation spectroscopy (HETCOR) offers a method to identify all directly bonded carbon–proton pairs in a molecule. This technique provides information from a ^1H NMR spectrum to aid in the assignment of ^{13}C NMR signals without prior knowledge of specific proton shift assignments.

Collection of X-ray Diffraction Data and Solution and Refinement of the Structure. Recrystallization from benzene gave crystals of the title compound suitable for X-ray diffraction studies. A crystal of the compound was loaded into a capillary tube under an argon atmosphere. The crystal was aligned, and intensity data were collected on a Nicolet R3m/v single-crystal X-ray diffractometer. Crystal, data collection, and refinement parameters are given in Table I.

Table I. Structure Determination Summary

Crystal Data	
empirical formula	$C_{40}H_{36}Ti$
color; habit	dark brown; parallelepiped
cryst size, mm	0.3 × 0.4 × 0.5
cryst syst	orthorhombic
space group	$P2_12_12_1$
unit cell dimens	
a, Å	8.447 (2)
b, Å	18.389 (4)
c, Å	19.210 (4)
V, Å^3	2984.0 (12)
Z	4
fw	564.6
density (calcd), Mg/m^3	1.257
abs coeff, mm^{-1}	0.308
F(000)	1192
Data Collection	
diffractometer used	Nicolet R3m/V
radiation	Mo Kα (λ = 0.71073 Å)
temp, K	293
monochromator	highly oriented graphite cryst
2θ range, deg	3.5–45.0
scan type	ω
scan speed, deg/min	variable; 3.97–14.68 in ω
scan range (ω), deg	1.20
bkgd measurement	stationary cryst and stationary counter at beginning and end of scan, each for 25.0% of total scan time
std rflns	3 measd every 100 rflns
index ranges	$0 \le h \le 9$, $0 \le k \le 19$, $0 \le l \le 20$
no. of rflns	2258
no. of indep rflns	2235
no. of obsd rflns	1782 ($F \ge 6.0\sigma(F)$)
abs cor	none
Solution and Refinement	
syst used	Nicolet SHELXTL PLUS (MicroVAX II)
soln	direct methods
refinement method	full-matrix least squares
quantity minimized	$\sum w(F_o - F_c)^2$
abs confign	not available
extinction cor	$\chi = 0.00030$ (11), where $F^* = F[1 + 0.002\chi F^2/(\sin 2\theta)]^{-1/4}$
H atoms	riding model, fixed isotropic *U*
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0002F^2$
final *R* indices (obsd data)	$R = 4.38\%$, $R_w = 4.82\%$
R indices (all data)	$R = 5.99\%$, $R_w = 5.02\%$
goodness of Fit	1.99
largest and mean Δ/σ	0.595, 0.003
data to param ratio	4.8:1
largest diff peak, e/Å^3	0.21
largest diff hole, e/Å^3	−0.19

Ti and some of the carbon atoms were located by direct methods, and the structure was developed by difference Fourier syntheses. A benzene molecule cocrystallizes with the complex. All hydrogen atoms were placed in idealized positions. No absorption correction was required (μ = 0.308 mm^{-1}). All non-hydrogen atoms were refined anisotropically. The correct enantiomer was chosen after refinement to convergence of both hands; the one with the lower *R* value was taken as the correct one.

All calculations used the SHELXTL program library (Nicolet Corp., Madison, WI). Table II gives the atomic coordinates, and Table III gives selected bond distances and angles. Additional crystallographic data are available as supplementary material.

Synthesis of 3,3-Bis(η^5-cyclopentadienyl)-4,5-diphenyl-3-titanatetracyclo[5.5.1.0^{2,6}.0^{8,12}]trideca-4,8,11-triene (I). A 100-mL, three-necked flask fitted with an argon adapter and rubber septa was filled with argon by a series of evacuate/fill cycles. To the flask was added 1.0 g (4.04 mmol) of titanocene dichloride, 0.10 g (4.1 mmol) of magnesium powder, 0.72 g (4.04 mmol) of diphenylacetylene, and a magnetic stirring bar. The flask was flushed with argon for 30 min, and 15 mL of freshly distilled tetrahydrofuran was injected through the septum. The

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Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)

	x	*y*	*z*	*U*(eq)[a]
Ti	1906 (1)	1609 (1)	6285 (1)	34 (1)
C(1)	5000 (8)	1369 (3)	7385 (3)	41 (2)
C(2)	3228 (8)	1192 (3)	7185 (3)	32 (2)
C(4)	981 (8)	2347 (3)	7077 (3)	33 (2)
C(5)	1254 (8)	2095 (3)	7717 (3)	33 (2)
C(6)	2294 (7)	1438 (3)	7851 (3)	32 (2)
C(7)	3631 (7)	1640 (4)	8384 (3)	40 (2)
C(8)	4553 (8)	964 (3)	8547 (3)	37 (2)
C(9)	4883 (9)	481 (3)	9036 (3)	48 (3)
C(10)	6053 (10)	−59 (4)	8748 (4)	58 (3)
C(11)	6357 (8)	211 (4)	8021 (4)	53 (3)
C(12)	5468 (8)	799 (3)	7922 (3)	40 (2)
C(13)	4810 (9)	2021 (4)	7894 (4)	49 (3)
C(14)	486 (12)	503 (5)	6561 (5)	66 (4)
C(15)	−556 (11)	1045 (5)	6623 (5)	63 (3)
C(16)	−781 (10)	1357 (4)	5985 (6)	73 (4)
C(17)	167 (14)	996 (6)	5500 (4)	87 (4)
C(18)	1004 (12)	478 (5)	5862 (6)	79 (4)
C(19)	4107 (13)	2392 (6)	6097 (4)	74 (4)
C(20)	2819 (14)	2704 (4)	5765 (5)	81 (4)
C(21)	2358 (10)	2242 (5)	5219 (4)	67 (3)
C(22)	3402 (11)	1663 (5)	5240 (4)	75 (4)
C(23)	4428 (11)	1748 (6)	5765 (5)	76 (4)
C(24)	−42 (8)	2988 (3)	6974 (3)	34 (2)
C(25)	−1663 (9)	2948 (4)	6969 (4)	59 (3)
C(26)	−2565 (8)	3557 (4)	6878 (5)	73 (4)
C(27)	−1935 (12)	4233 (4)	6803 (4)	66 (3)
C(28)	−329 (10)	4285 (4)	6821 (4)	59 (3)
C(29)	585 (9)	3681 (4)	6902 (4)	54 (3)
C(30)	548 (9)	2406 (4)	8354 (3)	49 (3)
C(31)	−642 (11)	2032 (5)	8688 (4)	78 (3)
C(32)	−1291 (17)	2282 (8)	9313 (5)	129 (7)
C(33)	−746 (21)	2897 (9)	9611 (6)	155 (9)
C(34)	439 (15)	3283 (6)	9277 (5)	118 (6)
C(35)	1058 (11)	3050 (4)	8639 (4)	78 (3)
C(36)	848 (14)	955 (7)	305 (7)	112 (6)
C(37)	−166 (15)	467 (7)	33 (5)	112 (6)
C(38)	−1157 (15)	96 (6)	447 (6)	108 (5)
C(39)	−1057 (14)	204 (6)	1110 (6)	107 (5)
C(40)	−74 (14)	683 (6)	1374 (6)	100 (5)
C(41)	862 (14)	1075 (6)	978 (7)	99 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Interatomic Distances and Angles with Standard Deviations for I

	(A) Bond Lengths (Å)		
Ti-C(2)	2.196 (6)	C(5)-C(6)	1.516 (9)
Ti-C(4)	2.184 (6)	C(5)-C(30)	1.476 (9)
Ti-Cp(Cent)	2.068	C(6)-C(7)	1.570 (8)
Ti-Cp′(Cent)	2.087	C(7)-C(8)	1.500 (9)
C(1)-C(2)	1.579 (9)	C(7)-C(13)	1.540 (9)
C(1)-C(12)	1.524 (9)	C(8)-C(9)	1.322 (9)
C(1)-C(13)	1.555 (9)	C(8)-C(12)	1.459 (9)
C(2)-C(6)	1.570 (8)	C(9)-C(10)	1.507 (10)
C(4)-C(5)	1.334 (9)	C(10)-C(11)	1.504 (10)
C(4)-C(24)	1.475 (9)	C(11)-C(12)	1.329 (10)
	(B) Bond Angles (deg)		
C(2)-Ti-C(4)	81.4 (2)	C(2)-C(6)-C(7)	103.8 (5)
Cp(Cent)-Ti-Cp′(Cent)	132.0	C(5)-C(6)-C(7)	109.8 (5)
Cp(Cent)-Ti-C(2)	106.5	C(6)-C(7)-C(8)	108.3 (5)
Cp′(Cent)-Ti-C(2)	110.0	C(6)-C(7)-C(13)	100.0 (5)
Cp(Cent)-Ti-C(4)	104.5	C(8)-C(7)-C(13)	99.7 (5)
Cp′(Cent)-Ti-C(4)	110.8	C(7)-C(8)-C(9)	144.5 (6)
Ti-C(2)-C(1)	127.0 (4)	C(7)-C(8)-C(12)	106.0 (5)
Ti-C(2)-C(6)	106.5 (4)	C(9)-C(8)-C(12)	109.5 (6)
C(1)-C(2)-C(6)	102.7 (4)	C(8)-C(9)-C(10)	108.6 (6)
Ti-C(4)-C(5)	111.4 (4)	C(9)-C(10)-C(11)	103.6 (6)
Ti-C(4)-C(24)	127.7 (4)	C(10)-C(11)-C(12)	107.7 (6)
C(5)-C(4)-C(24)	120.2 (6)	C(1)-C(12)-C(8)	106.1 (5)
C(4)-C(5)-C(6)	122.2 (5)	C(1)-C(12)-C(11)	143.3 (6)
C(4)-C(5)-C(30)	124.0 (6)	C(8)-C(12)-C(11)	110.6 (6)
C(6)-C(5)-C(30)	113.8 (5)	C(1)-C(13)-C(7)	95.8 (5)
C(2)-C(6)-C(5)	112.6 (5)		

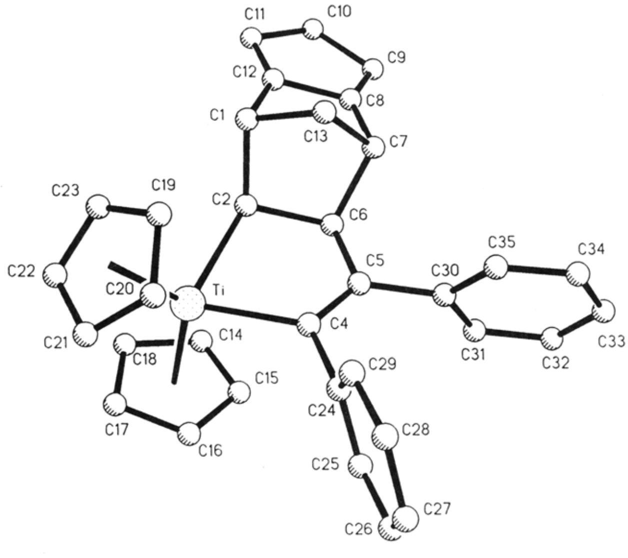

Figure 1. ORTEP labeling diagram for I.

flask was maintained at room temperature for 2.5 h, and 0.52 g (4.04 mmol) of tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene in 15 mL of THF was injected through the rubber septum. The reaction mixture was stirred for 2.5 h, during which time the color changed to purple. The solvent was removed under vacuum, and the flask was transferred to an argon-filled glovebox. The residue was dissolved in a minimum amount of dry benzene and the solution filtered through a pad of deactivated neutral alumina on a fritted funnel. The alumina was washed several times with benzene, and the combined filtrate and washings were concentrated to saturation. Dry hexane was added dropwise, with constant stirring, to obtain a purple powder. The liquid was decanted, and the powder was washed with pentane and dried under vacuum. The total yield of the compound was 0.78 g (39% yield based on Cp_2TiCl_2); mp 169–171 °C. Anal. Calcd for $C_{34}H_{30}Ti$: C, 83.97; H, 6.17. Found: C, 83.56; H, 6.29.

Crystals for X-ray analysis were obtained as follows. The compound was dissolved in a minimum amount of benzene, treated with hexane, and allowed to stand at room temperature under argon for several days, when crystals of the metallacycle were obtained. Additional crystals were obtained by allowing the decanted solution to stand in the refrigerator for several days.

Attempted Syntheses of Other Metallacyclo-2-pentenes. Methods identical with those described above were employed with Cp_2TiCl_2, the triene, and several disubstituted acetylenes such as bis(trimethylsilyl)acetylene, phenyl(trimethylsilyl)acetylene, 3-hexyne, 1-propyne, and dimethylacetylene dicarboxylate. With the last three acetylenes, products similar to I were not obtained; instead, the unreacted triene was recovered. However, in the case of bis(trimethylsilyl)acetylene and phenyl(trimethylsilyl)acetylene, the metallacyclopentadienes were isolated in low yields, formed from the cyclization of the respective acetylenes, and the triene was recovered unreacted.

In like manner, the cyclization of diphenylacetylene was attempted with norbornene and also with dicyclopentadiene. In neither case was any identifiable titanacyclo-2-pentene product obtained.

Results and Discussion

The synthesis of I was accomplished with use of information from the work of Vol'pin et al., who showed that "Cp_2Ti" reacts stepwise with disubstituted acetylenes. In that work, $Cp_2Ti(PhC{\equiv}CPh)$ was isolated and characterized as a titanacyclopropene ring and shown to react with a second molecule of a disubstituted alkyne to form titanacyclopentadienes.[17,18] Our method of synthesis of

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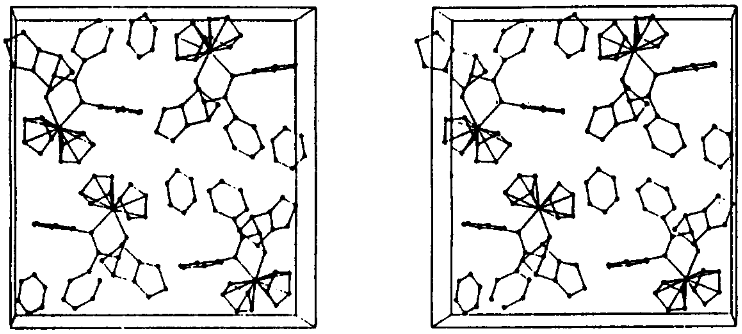

Figure 2. ORTEP packing diagram for I. The *a* axis points toward the viewer.

Scheme I

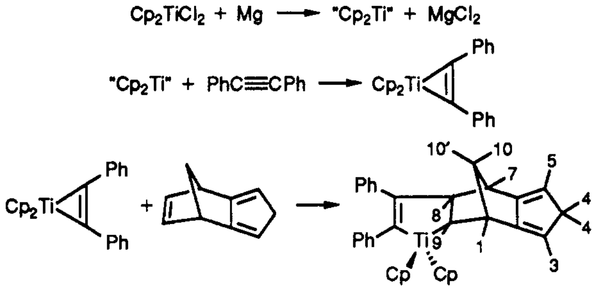

Table IV. ^1H and ^{13}C NMR Spectra of I[a]

H or C no.	δ(^1H), ppm	δ(^{13}C), ppm
1	3.34	48.56
2	...	149.64
3	5.61	115.37
4, 4'	3.14	45.56
5	5.4	109.63
6	...	143.82
7	2.96	42.78
8	3.41	55.49
9	1.78	83.93
10, 10'	2.65, 1.84	42.66
Cp_1	5.91	115.48
Cp_2	5.93	115.98
11		192
12		160.18
Ph	3 multiplets between 6.62 and 7.05	123.33, 125.26, 127.12, 127.44, 128.53, 128.74, 143.82, 139.63

[a] ^{13}C shifts are reported relative to the signal from residual C_6H_6 in the C_6D_6 solvent. Proton shifts are relative to TMS.

I was to allow reaction of equimolar amounts of "CpTi" with tolan, in which a color change occurs from red to brown, and then add an equimolar amount of the triene. This is shown in Scheme I, which also contains the proton numbering system with corresponding C numbers on which the following discussion of NMR spectral assignments is based.

The presence of two singlets at 5.91 and 5.93 ppm (10 protons) is assignable to the two sets of inequivalent Cp rings. To assign the other resonances, 2D COSY experiments were carried out. According to the numbering system shown in Scheme I, the following correlations were observed in the 2D-COSY NMR spectra: H_1 with $H_{10,10'}$ and H_3; H_3 with H_1 and $H_{4,4'}$; $H_{4,4'}$ with H_3 and H_5; H_5 with $H_{4,4'}$ and H_7; H_7 with $H_{10,10'}$ and H_5; H_8 with H_9; H_{10} with $H_{10'}$.

In order to assign the ^{13}C signals, HETCOR spectra were obtained. From direct correlation between the ^1H NMR signals, HETCOR gave the corresponding ^{13}C NMR spectral assignments. The ^1H and ^{13}C spectral assignments are given in Table IV. Complete copies of ^1H, ^{13}C, 2D-COSY, and HETCOR NMR spectra are available as supplementary material.

Compound I was characterized by X-ray diffraction techniques. Atomic coordinates and isotropic equivalent parameters for all non-hydrogen atoms are given in Table II. A drawing of I is shown in Figure 1, and important bond distances and angles are given in Table III.

The compound cocrystallizes with a benzene solvent molecule. The geometry around the titanium atom can be described as distorted tetrahedral with a (centroid)–Ti–(centroid)' angle of 132.0°, a C(2)–Ti–C(4) angle of 81.4°, (centroid)–Ti–C(2) angles of 106.5 and 110.0°, and (centroid)–Ti–C(4) angles of 104.5 and 110.8°. The Ti–(centroid) distances are 2.068 and 2.087 Å. The distances around the titana-2-cyclopentene ring are Ti–C(2) = 2.193 (6) Å, C(2)–C(6) = 1.571 (8) Å, C(6)–C(5) = 1.519 (9) Å, C(5)–C(4) = 1.334 (9) Å, and Ti–C(4) = 2.181 (6) Å. Consistent with the above bond distances, the angles at C(2) and C(6) are approximately tetrahedral while the angles at C(4) and C(5) are nearly trigonal. The titanacyclopentene portion of the structure is comparable to the analogous ring in the cobalta-2-cyclopentene complex mentioned earlier.[9] There is considerable distortion in the norbonyl ring system, and the cyclopentadiene appendage to the norbornyl ring is strictly planar; i.e., carbons C(1), C(7), C(8), C(9), C(10), C(11), and C(12) all lie in the same plane, as required by the sp^2 carbons C(8), C(9), C(11), and C(12). The two double bonds in the cyclopentadiene portion of the cyclized triene are still intact and therefore impervious to the cyclization reaction with titanium. Figure 2 shows the crystallographic packing of the molecule.

The synthesis of the unsymmetrically substituted titanacycle is of interest. In previous attempts to synthesize metallacyclopentadienes from stepwise addition of two different alkynes, only the symmetrical metallacyclopentadienes could be isolated.[19] Similarly, using alkynes other than tolan with the triene only led to titanacyclopentadienes or decomposition. We were also not successful in preparing titanacyclo-2-pentenes with tolan and norbornene or with tolan and dicyclopentadiene. Thus, the sole compound obtained in this investigation is the title compound, which is surprisingly stable, considering that analogous metallacyclo-2-pentenes could not be isolated.

Supplementary Material Available: Figures giving 2D COSY and HETCOR NMR spectra and tables of anisotropic temperature factors, complete bond lengths and bond angles, and calculated hydrogen atom positions (14 pages); a list of structure factors (8 pages). Ordering information is given on any current masthead page.

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(19) Sabade, M. B.; Farona, M. F.; Zarate, E. A.; Youngs, W. J. *J. Organomet. Chem.* **1988**, *338*, 347.