

# Titanacycles Derived from Reductive Coupling of Nitriles, Alkynes, Acetaldehyde, and Carbon Dioxide with Bis(pentamethylcyclopentadienyl)(ethylene)titanium(II)<sup>‡</sup>

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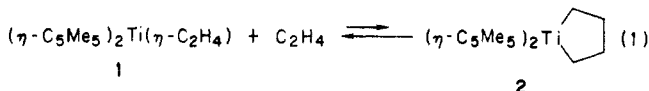
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Received October 3, 1984

The reactions of bis(pentamethylcyclopentadienyl)(ethylene)titanium(II),  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-C}_2\text{H}_4)$  (**1**), with alkynes, nitriles, carbon dioxide, and acetaldehyde have been examined and the products characterized spectroscopically. The most common reaction pathway observed is the addition of 1 equiv of substrate to **1** affording the respective monomeric metallacyclopentene  $(\eta\text{-C}_5\text{Me}_5)_2\text{TiC(R)=CMeCH}_2\text{CH}_2$  ( $\text{R} = \text{H}$  and  $\text{Me}$ ), metallacycloimine  $(\eta\text{-C}_5\text{Me}_5)_2\text{TiN=C(R)CH}_2\text{CH}_2$  ( $\text{R} = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $t\text{-C}_4\text{H}_9$ , and  $p\text{-CH}_3\text{C}_6\text{H}_4$ ), metallalactone  $(\eta\text{-C}_5\text{Me}_5)_2\text{TiOC(O)CH}_2\text{CH}_2$ , and oxymetallacyclopentane  $(\eta\text{-C}_5\text{Me}_5)_2\text{TiOCH(CH}_3\text{)-CH}_2\text{CH}_2$  products. In each case, the preferred (often exclusive) product from the reaction has the sterically least-hindered substituent adjacent to the titanium atom. Depending upon the reaction conditions and the particular substrate chosen, insertion into a C-H bond or substitution of the  $\text{C}_2\text{H}_4$  ligand in **1** by the substrate may be observed, as evidenced by the formation of  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti(C}\equiv\text{CR)(C}_2\text{H}_5)$ , where  $\text{R} = \text{CH}_3$  and  $t\text{-C}_4\text{H}_9$ , and  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-RC}\equiv\text{CR})$ , where  $\text{R} = \text{CH}_3$  and  $\text{C}_6\text{H}_5$ . Many of the Ti(IV) products are found to undergo further reactions under relatively mild conditions. For example, carbonylation of the metallacyclopentene  $(\eta\text{-C}_5\text{Me}_5)_2\text{TiC(CH}_3\text{)=C(CH}_3\text{)CH}_2\text{CH}_2$  quantitatively yields  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti(CO)}_2$  and the corresponding dimethylcyclopentenone while the metallacycloimine compounds  $(\eta\text{-C}_5\text{Me}_5)_2\text{TiN=C(R)CH}_2\text{CH}_2$  undergo a 1,3 hydrogen shift to generate metallacycloenamine species  $(\eta\text{-C}_5\text{Me}_5)_2\text{TiNHC(R)=CHCH}_2$ , where  $\text{R} = \text{CH}_3$  and  $\text{C}_2\text{H}_5$ . The latter rearrangement has been found to occur via an intramolecular pathway and is sensitive to the steric bulk of the R group.

## Introduction

We recently reported the synthesis and structure of bis(pentamethylcyclopentadienyl)(ethylene)titanium(II),  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-C}_2\text{H}_4)$  (**1**), together with some preliminary studies of its reactivity.<sup>1</sup> Displacement of the ethylene from **1** by good  $\pi$ -acceptor ligands such as CO and  $\text{CH}_3\text{NC}$  is observed, whereas treatment of **1** with  $\text{H}_2$  or HCl results in the liberation of ethane. Incorporation of ethylene in the organotitanium product was observed only in the case of the reversible reductive coupling of a second ethylene molecule, affording the titanacyclopentane  $(\eta\text{-C}_5\text{Me}_5)_2\text{TiCH}_2(\text{CH}_2)_2\text{CH}_2$  (**2**) (eq 1). The instability of **2**

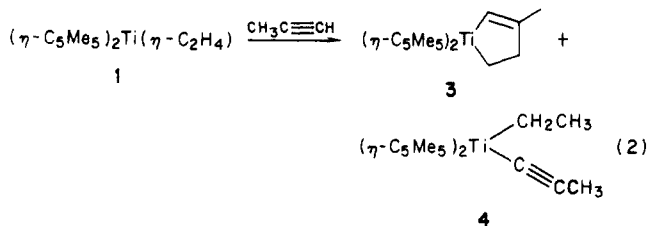


has precluded further study of this titanacyclopentane species, however. Since substrates having more reactive carbon-carbon multiple bonds or those with carbon-nitrogen or carbon-oxygen multiple bonds were expected to provide greater stability for the titanacyclic products derived from reductive coupling with the ethylene ligand, we have examined the reactions of **1** with alkynes, nitriles, acetaldehyde, and carbon dioxide. The results of these studies are reported herein.

## Results

**Reactions of  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-C}_2\text{H}_4)$  with Alkynes.** Compound **1** reacts rapidly with 1 equiv of propyne at  $-50^\circ\text{C}$ , affording approximately equal amounts of the metallacyclopentene complex  $(\eta\text{-C}_5\text{Me}_5)_2\text{TiCH=C(CH}_3\text{)-CH}_2\text{CH}_2$  (**3**) and the propynyl ethyl species  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti(C}\equiv\text{CCH}_3\text{)(CH}_2\text{CH}_3)$  (**4**). Spectroscopic data

$(\eta\text{-C}_5\text{Me}_5)_2\text{Ti(C}\equiv\text{CCH}_3\text{)(CH}_2\text{CH}_3)$  (**4**). Spectroscopic data



(IR **3**,  $\nu(\text{C}=\text{C})$  1587, **4**,  $\nu(\text{C}\equiv\text{C})$  2100  $\text{cm}^{-1}$ ; NMR, Tables I and II) are consistent with the structures shown in eq 2. The 2-methyl isomer of **3** is not observed, presumably due to unfavorable steric interactions between the methyl group and the  $[\text{C}_5\text{Me}_5]$  ligands.<sup>2</sup> Formation of **3** and **4** proceeds without loss of the ethylene ligand from **1**; addition of propyne to a solution of **1** containing 0.6 equiv of  $^{13}\text{CH}_2^{13}\text{CH}_2$  does not lead to incorporation of labeled ethylene in the products, either upon reaction at  $-50^\circ\text{C}$  or on standing several hours at  $25^\circ\text{C}$ . Over a period of several days at  $25^\circ\text{C}$ , the propynyl ethyl tautomer rearranges to **3** (eq 3). Hence, the reaction of **1** with propyne provides a quantitative, albeit rather slow route to **3**.

(1) (a) "Abstracts of Papers", 179th Meeting of the American Chemical Society, Houston, March 1980; American Chemical Society: Washington, D.C., 1980; PETR 27. (b) "Abstracts of Papers", 182nd National Meeting of the American Chemical Society, New York, 1981; American Chemical Society: Washington, D.C., 1981; IMOR 2950. (c) Cohen, S. A. Ph.D. Dissertation, California Institute of Technology, 1982. (d) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* 1983, 105, 1136-43.

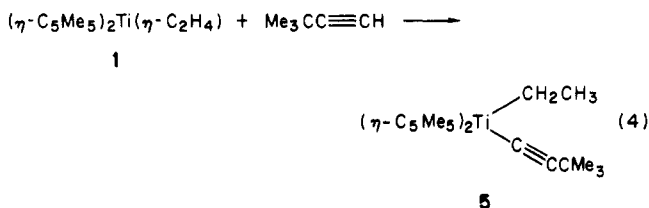
(2) (a) Application of recent theoretical results<sup>2b</sup> suggests the 3-methyltitanacyclopentene also is electronically favored over the 2-methyl isomer of **3**. The regiochemistry of the metallacyclopentenones derived from  $\text{CH}_2\text{C}\equiv\text{CR}$  remains unsettled; however, the regiospecific formation of the cycloimines, lactone, and oxycyclopentane (vide infra) also are in accord with this analysis. (b) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* 1980, 102, 2952-62.

<sup>‡</sup> Contribution No. 7103.

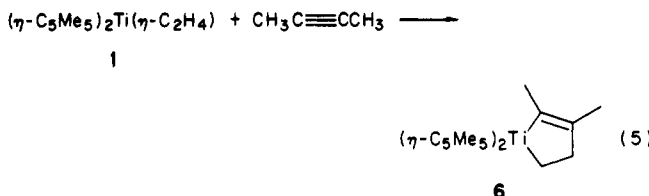


The titanacyclopentene complex **3** is also slowly obtained as the predominant product (80% pure by  $^1\text{H}$  NMR) from the reaction of **1** with allene at  $25^\circ\text{C}$ . The course of this reaction is not known; however, decamethyltitanocene-catalyzed isomerization of allene to propyne,<sup>3</sup> analogous to the catalytic isomerization of olefins by **1**,<sup>1</sup> may be a preliminary step.

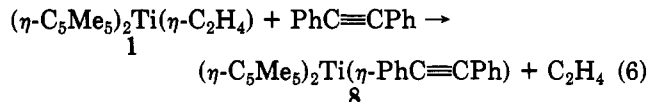
Treatment of a toluene solution of **1** with 1 equiv of  $\text{Me}_3\text{CC}\equiv\text{CH}$  at  $-40^\circ\text{C}$  quantitatively affords the *tert*-butylacetylide ethyl complex **5** (eq 4). Formation of the *tert*-butyl-substituted metallacyclopentene product analogous to **3** is not observed, either initially at  $-40^\circ\text{C}$  or after weeks at  $25^\circ\text{C}$ .



While the addition of terminal alkynes to **1** occurs rapidly at low temperatures, internal alkynes react more slowly with **1**. For example, the reaction with 2-butyne proceeds over a period of 8 h at  $25^\circ\text{C}$ , to afford a quantitative yield ( $^1\text{H}$  NMR) of  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2$  (**6**) (eq 5). Red-orange **6** is isolable as a



thermally stable, crystalline solid. Traces of free  $\text{C}_2\text{H}_4$  and the 2-butyne adduct  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-CH}_3\text{C}\equiv\text{CCH}_3)$  (**7**) are detected ( $^1\text{H}$  NMR) during the reaction of **1** with  $\text{CH}_3\text{C}\equiv\text{CCH}_3$ . Thermally unstable **7** may be independently prepared<sup>4</sup> by addition of 2-butyne to  $[(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}]_2(\mu\text{-N}_2)$ . Treatment of **1** with diphenylacetylene yields only  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-PhC}\equiv\text{CPh})$  (**8**) and  $\text{C}_2\text{H}_4$  (eq 6). No di-

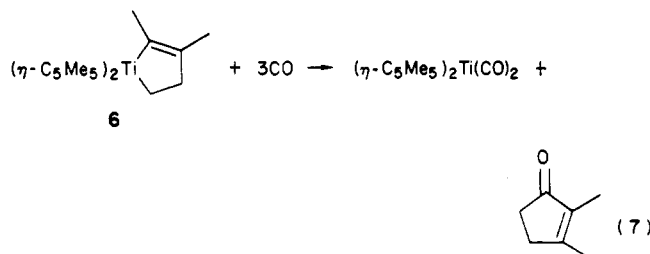


phenyltitanacyclopentene is formed, even at elevated temperatures under excess ethylene. Both **7** and **8** exhibit rather low  $\text{C}\equiv\text{C}$  stretching frequencies in the IR (**7**,  $\nu(\text{C}\equiv\text{C})$  1683, **8**,  $\nu(\text{C}\equiv\text{C})$  1647  $\text{cm}^{-1}$ ).

The reactions of **1** with the unsymmetrical internal alkynes 2-pentyne, 2-octyne, and 1-phenylpropyne also

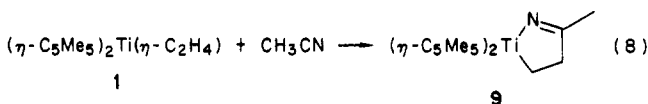
produces appreciable concentrations of the transient alkynyl adducts  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-CH}_3\text{C}\equiv\text{CR})$ , where  $\text{R} = \text{CH}_2\text{CH}_3$ ,  $\text{CH}_2(\text{CH}_2)_3\text{CH}_3$ , and  $\text{Ph}$ , prior to formation of the corresponding titanacyclopentenenes. The final products have been characterized only by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrometry, and in each case the titanacyclopentene appears to be present as a mixture of the 2-methyl and 3-methyl isomers.<sup>5</sup>

Carbonylation (3 atm) of **6** occurs within 18 h at  $80^\circ\text{C}$  to afford  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{CO})_2$ <sup>6</sup> and 2,3-dimethylcyclopent-2-enone<sup>7</sup> quantitatively by  $^1\text{H}$  NMR (eq 7). Unfortu-

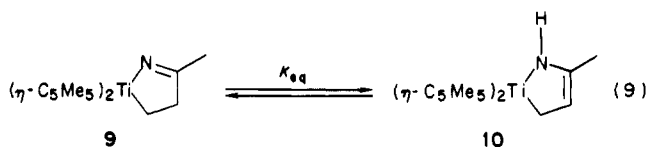


nately,  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{CO})_2$  is unreactive toward  $\text{C}_2\text{H}_4$  and/or  $\text{CH}_3\text{C}\equiv\text{CCH}_3$ , even under forcing conditions, so that a catalytic synthesis of 2,3-dimethylcyclopent-2-enone based on this chemistry has not yet been achieved.<sup>8</sup>

**Reactions of  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-C}_2\text{H}_4)$  with Nitriles.** Addition of 1 equiv of acetonitrile to a toluene solution of **1** at  $-50^\circ\text{C}$  results in quantitative formation of the metallacycloimine complex  $(\eta\text{-C}_5\text{Me}_5)_2\text{TiN}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2$  (**9**) (eq 8). Red-orange **9** has been characterized



by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrometry (Tables I and II) and infrared spectroscopy ( $\nu(\text{C}=\text{N})$  1638  $\text{cm}^{-1}$ ). Above  $-10^\circ\text{C}$  an equilibrium is established between **9** and its metallacycloenamine tautomer **10** (equ 9). The value of  $K_{\text{eq}}$  varies



from  $\sim 0.4$  at  $0^\circ\text{C}$  to  $\sim 0.8$  at  $25^\circ\text{C}$ . The specificity of this 1,3 hydrogen shift is apparent from the fact that  $(\eta\text{-C}_5\text{Me}_5)_2\text{TiN}=\text{C}(\text{CD}_3)\text{CH}_2\text{CH}_2$ , prepared from **1** and

(3) (a) Schwartz, J.; Hart, D. W.; McGiffert, B. *J. Am. Chem. Soc.* 1974, 96, 5613-4. (b) McGrady, N. D.; McDade, C.; Bercaw, J. E. In "Organometallic Compounds: Synthesis, Structure, and Theory"; B. L. Shapiro, Ed.; Texas A & M Press: College Station, TX, 1983; pp 46-85. (c) Doherty, N. M. Ph.D. Dissertation, California Institute of Technology, 1984. (d) McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* 1985, 279, 281-315.

(4) (a) Threlkel, R. S. Ph.D. Dissertation, California Institute of Technology, 1980. (b) Spectroscopic data for **7**: NMR, Tables I and II; IR (Nujol mull) 2705 (w), 1683 (w), 1495 (m), 1100 (m), 1025 (s), 800 (m), 595 (s), 425 (s), 360 (m)  $\text{cm}^{-1}$ .

(5) (a) Ratio of the isomeric 2-methyl- and 3-methyl-substituted metallacyclopentenenes derived from **1** and 2-pentyne is 80:20, from 2-octyne, 85:15, from 1-phenylpropyne,  $\leq 5:95$  (spectroscopic data suggest that the major isomer may be the 2-phenyl-3-methyltitanacyclopentene but this has not been confirmed). (b) Limited spectroscopic data for  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-CH}_3\text{C}\equiv\text{CR})$  and the isomeric metallacyclopentenenes are available as supplementary material.

(6) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* 1972, 94, 1219-38.

(7) Berkowitz, W. F.; Ozorio, A. A. *J. Org. Chem.* 1971, 36, 3787-92 and references therein.

(8) (a) The carbon monoxide insertion/reductive elimination behavior of **6** differs significantly from that of **2**<sup>1,5b</sup> or from the reactivity of zirconocene<sup>8c,d</sup> and decamethylzirconocene<sup>8b,d,9e</sup> complexes. The reactivity of **6** and CO is typical of other dialkyl- or diaryltitanocene derivatives, however.<sup>8b,f,g</sup> (b) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* 1976, 98, 6529-35 and references therein. (c) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc. Dalton Trans.* 1977, 1946-50. (d) Erker, G.; Kropp, K. *J. Organomet. Chem.* 1980, 194, 45-60. (e) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* 1978, 100, 2716-24. (f) Masai, H.; Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* 1968, 41, 750-1. (g) Fachinetti, G.; Floriani, C. *J. Chem. Soc. Chem. Commun.* 1972, 654-5.

Table I. Proton NMR Data

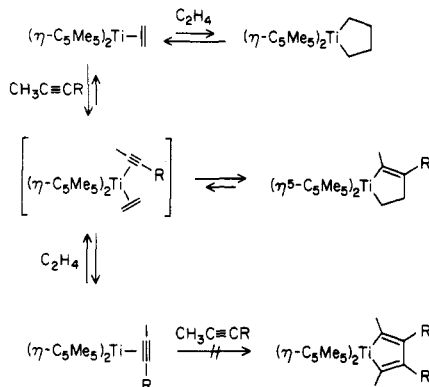
compd (solv and temp) <sup>a</sup>	assign <sup>t</sup>	chem shift, $\delta$	mult <sup>b</sup>	$J(\text{H-H})$ , Hz
$(\eta\text{-C}_5\text{Me}_5)_2\text{TiCH}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2$ $(\text{C}_6\text{D}_6)$	3	a 1.76 b 0.83 c 2.21 d 4.90 e 1.60	s t t (br) q dt	7.5 7.5 1.0 1.0, 1.0
$(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{CH}_2\text{CH}_3)(\text{C}\equiv\text{CCH}_3)$ $(\text{C}_6\text{D}_6)$	4	a 1.90 b 0.57 c 1.15 d 1.68	s q t s	7.5 7.5
$(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{CH}_2\text{CH}_3)[\text{C}\equiv\text{CC}(\text{CH}_3)_3]$ $(\text{C}_6\text{D}_6)$	5	a 1.88 b 0.41 c 1.40 d 1.23	s q t s	7.0 7.0
$(\eta\text{-C}_5\text{Me}_5)_2\text{TiC}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2$ $(\text{C}_6\text{D}_6)$	6	a 1.80 b 1.06 c 2.13 d 1.03 e 1.43	s t t (br) tq q	7.4 7.4 0.9, 0.9 0.9
$(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-CH}_3\text{C}\equiv\text{CCH}_3)$ $(\text{C}_6\text{D}_{12})$	7	a 1.89 b 1.74	s s	
$(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)$ $(\text{C}_6\text{D}_{12})$	8	a 1.74 b 6.80 c 6.54 d 6.86	s m d d	8.0 8.0
$(\eta\text{-C}_5\text{Me}_5)_2\text{TiN}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2$ $(\text{C}_7\text{D}_8, 0^\circ\text{C})$	9	a 1.82 b 0.63 c 3.33 d 1.57	s t t s	7.0 7.0
$(\eta\text{-C}_5\text{Me}_5)_2\text{TiNHC}(\text{CH}_3)=\text{CHCH}_2$ $(\text{C}_7\text{D}_8, 0^\circ\text{C})$	10	a 1.72 b 1.05 c 5.03 d 6.19 e 1.81 (obsd in $^2\text{H}$ spectrum)	s t t s	6 6 72 <sup>c</sup>
$(\eta\text{-C}_5\text{Me}_5)_2\text{TiN}=\text{C}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2$ $(\text{C}_6\text{D}_6)$	11	a 1.83 b 0.68 c 3.32 d 1.12 e 0.92	s t t q t	7.3 7.3 7.0 7.0
$(\eta\text{-C}_5\text{Me}_5)_2\text{TiN}=\text{C}(\text{CMe}_3)\text{CH}_2\text{CH}_2$ $(\text{C}_7\text{D}_8)$	12	a 1.80 b 0.48 c 3.43 d 1.01	s t t s	7.1 7.1
$(\eta\text{-C}_5\text{Me}_5)_2\text{TiN}=\text{C}(\text{C}_6\text{H}_4\text{CH}_3)\text{CH}_2\text{CH}_2$ $(\text{C}_7\text{D}_8)$	13	a 1.83 b 0.68 c 3.88 d 2.11 e 6.91 f 7.38	s t t s d d	7.1 7.1 8.3 8.3
$(\eta\text{-C}_5\text{Me}_5)_2\text{TiNHC}(\text{CH}_2\text{CH}_3)=\text{CHCH}_2$ $(\text{C}_6\text{D}_6)$	14	a 1.73 b (not observed) c 5.12 d 6.43 e 2.13 f (not observed)	s t s q	4 7
$(\eta\text{-C}_5\text{Me}_5)_2\text{TiOC}(\text{O})\text{CH}_2\text{CH}_2$ $(\text{C}_7\text{D}_8)$	15	a 1.67 b 1.09 c 3.24	s t t	8.0 8.0

Table I (Continued)

compd (solv and temp) <sup>a</sup>	assignt	chem shift, $\delta$	mult <sup>b</sup>	$J(\text{H-H})$ , Hz
$(\eta\text{-C}_5\text{Me}_5)(\eta\text{-C}_5\text{Me}_5)_2\text{TiOCH}(\text{CH}_3)\text{CHH}'\text{CHH}'$ 16 <sub>a                      b                      c      d      ef      gh</sub> $(\text{C}_7\text{D}_8)$	a	1.85	s	
	b	1.82	s	
	c	4.71	dqd	11.0, 6.1, 3.7
	d	0.95	d	6.1
	e	2.67	dddd	12.2, 12.2, 11.0, 7.3
	f	2.43	dddd	12.2, 7.3, 3.7, 1.2
H' cis to methine H	g	0.23	ddd	11.0, 7.3, 1.2
	h	2.17	ddd	12.2, 11.0, 7.3

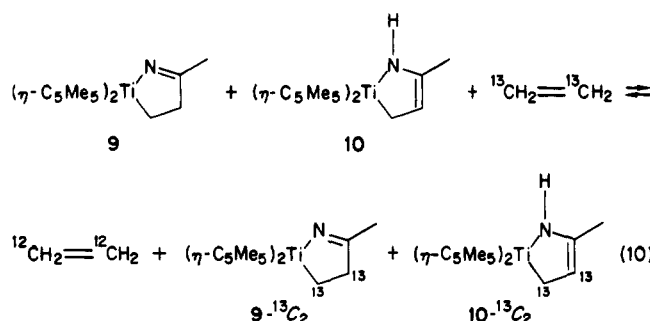
<sup>a</sup> Sample temperature 34 °C unless given. <sup>b</sup> s = singlet, d = doublet, t = triplet, q = quartet, br = broad. <sup>c</sup>  $^1J(^{15}\text{N-H})$ .

Scheme I



$\text{CD}_3\text{CN}$ , yields only  $(\eta\text{-C}_5\text{Me}_5)_2\text{TiNHC}(\text{CD}_3)=\text{CHCH}_2$ . Moreover, no H-D scrambling is observed after 2 days at 25 °C ( $^2\text{H}$  NMR).

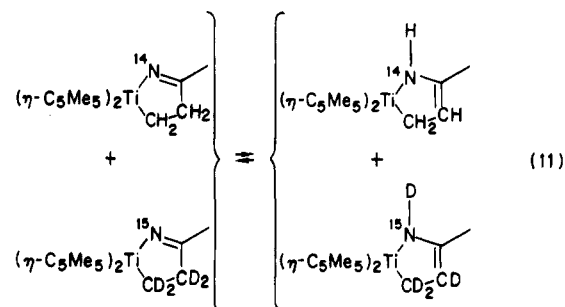
Carbon-carbon bond formation in the generation of 9, substantiated by the  $^{13}\text{C}$ - $^{13}\text{C}$  coupling constants observed for  $^{13}\text{C}$ -labeled 9 (Table II), is found to be reversible. Thus, while incorporation of  $^{13}\text{CH}_2^{13}\text{CH}_2$  into 9 is not detected ( $^1\text{H}$  and  $^{13}\text{C}$  NMR) when addition of  $\text{CH}_3\text{CN}$  to 1 is carried out at -50 °C in the presence of 1 equiv of  $^{13}\text{CH}_2^{13}\text{CH}_2$ , unenriched ethylene and  $^{13}\text{C}_2$ -labeled 9 and 10 are slowly formed at 25 °C, demonstrating that ethylene exchange occurs subsequent to the formation of 9 and 10 (eq 10).



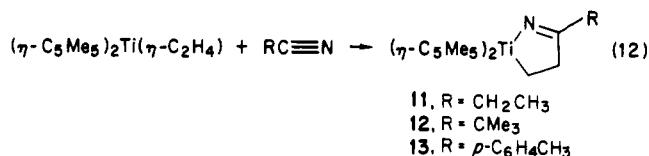
The lability of the ethylene is likely responsible for the rapid decomposition that occurs when solutions of 9 and 10 are heated above 40 °C or exposed to  $\text{CO}$ , excess  $\text{CH}_3\text{CN}$ , or vacuum above -20 °C. In each case,  $\text{C}_2\text{H}_4$  is produced along with a mixture of as yet unidentified organotitanium compounds.

As a solid, 9 can be stored for months at -20 °C and handled for brief periods at 25 °C without decomposition or formation of 10. Thus, it proved possible to address the molecularity of the isomerization of 9 to 10 with a crossover experiment. A toluene solution of doubly labeled  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}^{15}\text{N}=\text{C}(\text{CH}_3)\text{CD}_2\text{CD}_2$  (9- $^{15}\text{N}, d_4$ ) and unlabeled 9 ( $[9\text{-}^{15}\text{N}, d_4]/[9] = 1.2 \pm 0.4$ ) was warmed to 0 °C, and the

9  $\rightleftharpoons$  10 tautomerization was monitored by  $^1\text{H}$  NMR spectrometry. The extent of conversion of 9 to 10 was indicated by their respective  $\text{C}_5\text{Me}_5$  intensities and the extent of crossover determined from the intensities of the  $^{14}\text{N-H}$  and  $^{15}\text{N-H}$  resonances ( $^1J(^{15}\text{N-H}) = 72$  Hz for 10- $^{15}\text{N}$ ). Although some decomposition is detected (ca. 3%) during the latter stages of the experiment, the extent of H-D scrambling observed in the products (column 5, Table III) remains small as equilibrium between 9 and 10 is reached. Thus the imine  $\rightleftharpoons$  enamine tautomerization appears to proceed predominantly in an intramolecular fashion (eq 11).

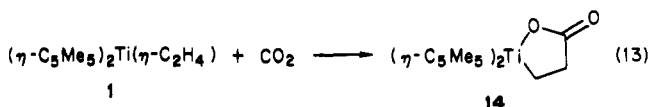


Propionitrile, 2,2-dimethylpropionitrile, and *p*-tolunitrile also react rapidly with 1 to yield the corresponding titanacycloimines (eq 12). The infrared and NMR spectra



of 11, 12, and 13 closely resemble those of 9 but, unlike 9, these derivatives proved sufficiently stable in the solid state for full characterization. The ethyl-substituted titanacycloimine complex 11 tautomerizes slowly to a small extent ( $K_{\text{eq}} = 0.10$  at 25 °C), yielding  $(\eta\text{-C}_5\text{Me}_5)_2\text{TiNHC}(\text{C}_2\text{H}_5)=\text{CHCH}_2$  (14), which has been characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrometry. No isomerization ( $K_{\text{eq}} < 0.01$ ) of 12 or 13 is observed even after several weeks at 25 °C.

**Reactions of  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-C}_2\text{H}_4)$  with Carbon Dioxide and Acetaldehyde.** Addition of 1 equiv of  $\text{CO}_2$  to a toluene solution of 1 at -78 °C rapidly affords the bright red titanalactone  $(\eta\text{-C}_5\text{Me}_5)_2\text{TiOC}(\text{O})\text{CH}_2\text{CH}_2$  (15) in high yield (eq 13). Monomeric 15 exhibits a  $\nu(\text{CO})$  at



1653  $\text{cm}^{-1}$  in its infrared spectrum for the uncoordinated



Table II (Continued)

compd (solv and temp) <sup>a</sup>	assignt	chem shift, $\delta$	$^1J(\text{C-H})$ (m), <sup>b</sup> Hz	$^1J(\text{C-C})$ , <sup>c</sup> Hz	$^xJ(\text{C-H})$ (m), <sup>d</sup> Hz
$(\eta\text{-C}_5\text{Me}_5)_2\text{TiN}=\text{C}(\text{C}_6\text{H}_4\text{CH}_3)\text{CH}_2\text{CH}_2$ $\begin{matrix} \text{a} & \text{b} & & \text{e} & \text{f-i} & \text{j} & & \text{d} & \text{c} \end{matrix}$	13	a b c d e f g h i j	120.2 12.0 42.7 55.7 161.8 120.9 126.4 128.9 137.0 21.3	(s) 126 (q) 122 (t) 122 (t) (s) (s) 158 (d) 160 (d) (s) (obscured)	33 (cd)
(C <sub>6</sub> D <sub>12</sub> ; C <sub>7</sub> D <sub>8</sub> for $^{13}\text{C}\{^1\text{H}\})$					
$(\eta\text{-C}_5\text{Me}_5)_2\text{TiNHC}(\text{CH}_2\text{CH}_3)=\text{CHCH}_2$ $\begin{matrix} \text{a} & \text{b} & & \text{e} & \text{f} & \text{g} & & \text{d} & \text{c} \end{matrix}$ (C <sub>7</sub> D <sub>8</sub> )	14	a b c d e f g	116.9 11.6 61.2 112.5 142.2 34.1 10.4		38 (cd)
$(\eta\text{-C}_5\text{Me}_5)_2\text{TiOC}(\text{O})\text{CH}_2\text{CH}_2$ $\begin{matrix} \text{a} & \text{b} & & \text{e} & & & & \text{d} & \text{c} \end{matrix}$ (C <sub>6</sub> D <sub>6</sub> )	15	a b c d e	124.1 11.6 54.0 53.6 171.5	(s) 126 (q) 128 (t) 125 (t) (s)	52 (de) 6 (t)
$(\eta\text{-C}_5\text{Me}_5)(\eta\text{-C}_5\text{Me}_5)\text{TiOC}(\text{CH}_3)\text{CH}_2\text{CH}_2$ $\begin{matrix} \text{a} & \text{c} & & \text{b} & \text{d} & & \text{g} & \text{h} & \text{f} & \text{e} \end{matrix}$ (C <sub>6</sub> D <sub>6</sub> )	16	a b c d e f g h	121.3 121.0 12.1 12.2 55.8 52.7 75.8 25.9	(s) (s) 126 (q) 126 (q) 121 (t) 127 (t) 138 (d) 124 (q)	31 (ef) 4 (d)

<sup>a</sup> Sample temperature 34 °C unless given. <sup>b</sup> s = singlet, d = doublet, t = triplet, q = quartet, br = broad. <sup>c</sup> (xy) refers to carbon assignments. <sup>d</sup> Long-range C-H coupling values. <sup>e</sup> Long-range C-C coupling values.

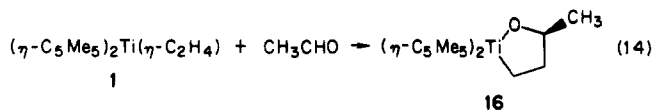
Table III. Results of the Imine  $\rightleftharpoons$  Enamine Crossover Experiment

time, min	[10]/[9]	extent of equilibratn <sup>a</sup>	[10- $^{15}\text{NH}$ ]/[10- $^{14}\text{NH}$ ]	extent of scrambling <sup>b</sup>
0	<0.02	<0.05	<<0.05	
15	0.07 (4)	0.19	<0.05	<0.04
34	0.22 (3)	0.56	0.07 (4)	0.06
83	0.27 (2)	0.68	0.12 (4)	0.10
440	0.35 (2)	0.90	0.27 (3)	0.23

<sup>a</sup> [10]/[9]/ $K_{\text{eq}}$ , where  $K_{\text{eq}} = 0.39 \pm 0.02$  at 0 °C. <sup>b</sup> [10- $^{15}\text{NH}$ ]/[10- $^{14}\text{NH}$ ]/ $S_{\text{eq}}$ , where  $S_{\text{eq}} = 1.2 \pm 0.4$  (statistical scrambling ratio from initial [9- $^{15}\text{N}$ ,  $d_4$ ]/[9], ignoring thermodynamic isotope effects).

carbonyl. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are readily assigned, and the  $^{13}\text{C}$ - $^{13}\text{C}$  coupling constant of 52 Hz between the  $\beta$ -methylene carbon and carbonyl carbon of  $(\eta\text{-C}_5\text{Me}_5)_2\text{TiO}^{13}\text{C}(\text{O})^{13}\text{CH}_2\text{CH}_2$  clearly establishes the formation of the C-C bond of 15 (Table II). Compound 15 is thermally robust as a solid and in solution but decomposes slowly upon exposure to visible light. When carried out above 0 °C, the carboxylation of 1 ( $\text{CO}_2:1 = 1$ ) does not produce 15; rather ethylene is liberated, and an unidentified light-colored precipitate is formed.

Acetaldehyde reacts rapidly with 1 below -20 °C to yield the oxytitanacyclopentane complex  $(\eta\text{-C}_5\text{Me}_5)_2\text{TiOCH}(\text{CH}_3)\text{CH}_2\text{CH}_2$  (16) (eq 14). The 90-MHz  $^1\text{H}$  NMR



spectrum for 16 is consistent with the structure shown,

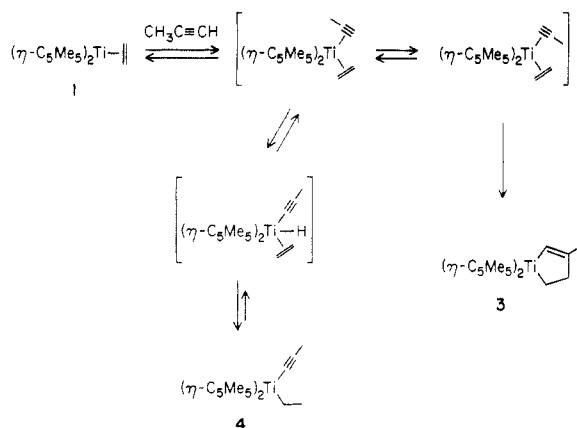
having two resonances assignable to the two inequivalent  $[\text{C}_5\text{Me}_5]$  ligands and a doublet for the methyl substituent. At 500 MHz, the six highly coupled hydrogen resonances of the  $\text{TiOCH}(\text{CH}_3)\text{CCH}'\text{CHH}'$  moiety are resolved (Table I). The infrared and  $^{13}\text{C}$  NMR spectra also support the formulation of 16. Bright orange-red 16 is quite stable, and there is no indication of formation of the tautomeric acyl ethyl complex  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{COCH}_3)(\text{CH}_2\text{CH}_3)$  even after several days at 25 °C.

The reaction of 1 with acetone differs considerably from that of 1 with acetaldehyde and does not afford a 3,3-dimethyloxytitanacyclopentane species analogous to 16. No reaction between 1 and 1 equiv of  $(\text{CH}_3)_2\text{CO}$  is observed below 0 °C. At 25 °C, evolution of ethylene accompanies the reaction. Unreacted 1 and a mixture of unidentified organotitanium products remain in solution.

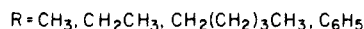
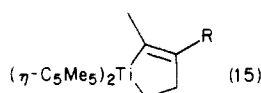
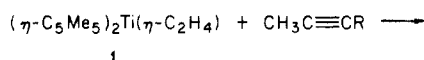
## Discussion

Bis(pentamethylcyclopentadienyl)(ethylene)titanium (1) reacts with a variety of unsaturated organic compounds.

Scheme II



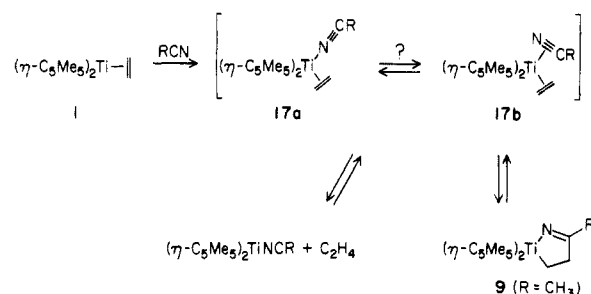
The reactions of 1 with 2-butyne and several other methyl-substituted internal alkynes proceed analogously to the reaction of 1 with ethylene (eq 1), affording 2,3-disubstituted titanacyclopentenes (eq 15). Displacement of the



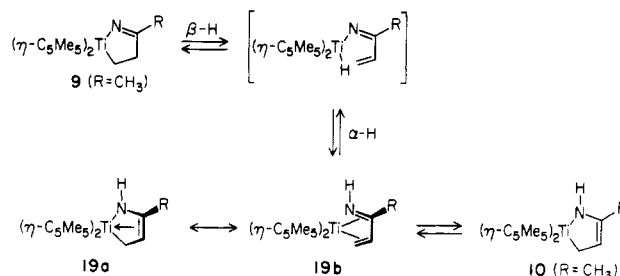
ethylene ligand of 1 by methyl-substituted internal alkynes also occurs and competes effectively with the reductive coupling pathway, since acetylene adducts and ethylene are detected by NMR as transient species.<sup>9</sup> With diphenylacetylene, only the simple displacement of ethylene is observed, yielding the very stable adduct  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-PhC}\equiv\text{CPh})$ . We believe that the steric bulk and the electron-withdrawing capability of the phenyl substituents of  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-PhC}\equiv\text{CPh})$  prevent formation of the 2,3-diphenyltitanacyclopentene. Effectively, the titanium is more "oxidized" in  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-PhC}\equiv\text{CPh})$  than are the metal centers in  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-CH}_3\text{C}\equiv\text{CR})$ , where  $\text{R} = \text{CH}_3$ ,  $\eta\text{-C}_5\text{H}_{11}$ , and  $\text{Ph}$ . In this regard, it is interesting that reductive coupling of 2 equiv of alkyne by decamethyltitanocene is not observed,<sup>4</sup> even at elevated temperatures in the presence of excess alkyne, whereas for both the parent  $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}]^{10}$  and decamethylzirconocene<sup>4</sup> systems, very stable metallacyclopentadiene derivatives are typically obtained. Apparently, a delicate balancing of electronic and steric effects for the decamethyltitanocene system makes the 2-methyltitanacyclopentene compounds much preferred over both the titanacyclopentane and titanacyclopentadiene products (Scheme I).

With terminal alkynes, insertion into the C-H bond may be exclusive pathway as observed with  $\text{Me}_3\text{CC}\equiv\text{CH}$  (eq 4), or it may be competitive with reductive coupling as observed with propyne (eq 2). Isomerization of the propynyl ethyl complex to the 3-methyltitanacyclopentene occurs under more forcing conditions, suggesting parallel pathways for the reaction of 1 and  $\text{CH}_3\text{C}\equiv\text{CH}$ , with 3 the

Scheme III



Scheme IV



thermodynamically favored product (Scheme II).

Rapid reductive coupling of nitriles, acetaldehyde, and carbon dioxide with  $(\eta\text{-C}_5\text{Me}_5)_2\text{Ti}(\eta\text{-C}_2\text{H}_4)$  also is observed. Formation of strong Ti-N or Ti-O bonds in the five-membered-ring products undoubtedly provides much of the driving force for these reactions. Although 1 and  $\text{CH}_3\text{CN}$  directly afford 9 by an associative pathway, the slow incorporation of  $^{13}\text{C}_2\text{H}_4$  into the titanacycloimine ring suggests that the reductive coupling reaction is reversible and that ethylene may be lost to solution from a nitrile-ethylene intermediate 17, as shown in Scheme III. Such behavior is reminiscent of the reactivity of 1 with alkynes (vide supra) and suggests that the nitrile is  $\eta^2$ -coordinated (17b), at least in the nitrile-ethylene adduct that couples to the titanacycloimine product.<sup>2</sup> The end-on  $\eta^1$  isomer 17a is a reasonable alternative structure by analogy to  $\eta^1\text{-N}_2$  adducts of decamethyltitanocene<sup>11</sup> but appears less likely than 17b to afford 9.<sup>12</sup>

Isomerization of the metallacycloimine complexes to equilibrium mixtures of  $(\eta\text{-C}_5\text{Me}_5)_2\text{TiN}=\text{C(R)CH}_2\text{CH}_2$  and  $(\eta\text{-C}_5\text{Me}_5)_2\text{TiNHC(R)=CHCH}_2$  occurs for  $\text{R} = \text{CH}_3$  and  $\text{C}_2\text{H}_5$  but not for  $\text{R} = \text{CMe}_3$  or  $p\text{-CH}_3\text{C}_6\text{H}_4$ , suggesting that steric rather than electronic effects are the determining factor. The imine  $\rightleftharpoons$  enamine tautomerization is a 1,3 hydrogen shift and thus a symmetry-forbidden reaction. Such tautomerizations are, however, commonly catalyzed by even traces of acid or base.<sup>13</sup> Significantly, the results of the crossover experiment (Table III) indicate that the  $9 \rightleftharpoons 10$  isomerization occurs *intramolecularly*. Although there is little additional evidence that bears directly on the mechanism of this transformation, we believe the observations are best accommodated by a sequence involving intramolecular, titanium-mediated, reversible hydrogen eliminations from the  $\beta$ -methylene carbon of the

(9) Similar behavior has been reported for Ta(olefin) complexes: Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. I. *Inorg. Chem.* 1981, 20, 387-98.

(10) (a) Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* 1966, 39, 1178-82. (b) Mattia, J.; Sikora, D. J.; Macomber, D. W.; Rausch, M. D.; Hickey, J. P.; Friesen, G. D.; Todd, L. J. *J. Organomet. Chem.* 1981, 213, 441-50 and references therein. (c) Demerseman, B.; Dixneuf, P. H. *J. Chem. Soc. Chem. Commun.* 1981, 665-6.

(11) Sanner, R. D.; Duggan, D. M.; McKenzie, T. C.; Marsh, R. E. Bercaw, J. E. *J. Am. Chem. Soc.* 1976, 98, 8358-65.

(12) (a) Reversible oxidative coupling of two nitriles by  $(\eta\text{-C}_5\text{Me}_5)\text{Zr}^{\text{II}}$  has been found to be facile. (b) Wolczanski, P. T. Ph.D. Dissertation, California Institute of Technology, 1981.

(13) (a) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; Harper Row: New York, 1976. (b) March, J. "Advanced Organic Chemistry"; McGraw-Hill: New York, 1977. (c) Dykes, S. F. "The Chemistry of Enamines"; University Press: Cambridge, 1973.

imine and from the  $\alpha$ -nitrogen of the enamine (Scheme IV).<sup>14</sup>

### Experimental Section

**General Considerations.** All manipulations were performed by using glovebox or high vacuum line techniques. Argon, nitrogen, and hydrogen were purified by passage over MnO on vermiculite and activated Linde 4Å molecular sieves. Solvents were purified by vacuum transfer, first from LiAlH<sub>4</sub> and then "titanocene".<sup>6</sup> Benzene-*d*<sub>6</sub>, cyclohexane-*d*<sub>12</sub>, and toluene-*d*<sub>8</sub> (Aldrich, Stohler) were dried over molecular sieves and vacuum transferred from "titanocene". Propyne, 2-butyne, 2-pentyne, 3,3-dimethyl-1-butyne (all Farchan), ethylene, allene, and acetaldehyde were freeze-pump-thaw degassed at -196 °C. Methyl iodide, CD<sub>3</sub>CN (99% D, Kor), <sup>13</sup>CH<sub>3</sub>CN (90% <sup>13</sup>C, Stohler), and all other nitriles were vacuum transferred from CaH<sub>2</sub>. Acetonitrile-*d*<sub>3</sub> and CH<sub>3</sub>C<sup>15</sup>N were prepared by addition of methyl iodide to a toluene solution containing 18-crown-6 and Na<sup>13</sup>CN (91.5% <sup>13</sup>C, Prochem) or KC<sup>15</sup>N (99% <sup>15</sup>N, Koch), respectively.<sup>17</sup> Carbon dioxide and carbon monoxide were used directly from the cylinder. Ethylene-<sup>13</sup>C<sub>2</sub> (90% <sup>13</sup>C, Merck, Sharp, and Dohme) and ethylene-*d*<sub>4</sub> (98% D, Stohler) were freeze-pump-thaw degassed at -196 °C and distilled at -78 °C. Acetone and 1-phenylpropyne were distilled from molecular sieves; diphenylacetylene was recrystallized from diethyl ether. [( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti]<sub>2</sub>( $\mu$ -N<sub>2</sub>), ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti( $\eta$ -C<sub>2</sub>H<sub>4</sub>),<sup>1</sup> ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti( $\eta$ -<sup>13</sup>C<sub>2</sub>H<sub>4</sub>),<sup>1</sup> and ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti( $\eta$ -C<sub>2</sub>D<sub>4</sub>)<sup>1</sup> were prepared by previously reported methods.

Proton, <sup>2</sup>H, and <sup>13</sup>C NMR spectra were recorded by using Varian EM-390, JEOL FX90Q and Bruker WM-500 spectrometers. Spectra were taken in benzene or toluene solutions, and data are referenced to Me<sub>4</sub>Si at  $\delta$  0. Infrared spectra were obtained by using a Beckman 4240 spectrophotometer. Spectra of solids were recorded as Nujol mulls using KBr plates; spectra of gases were measured by using a 10-cm path-length cell (NaCl windows) fitted with a stopcock and ball joint for attachment to the vacuum line. Molecular weights were determined cryoscopically or by vapor-phase osmometry. Elemental analyses were performed by Alfred Bernhardt Analytical Laboratories, Germany.

**Procedure.** A majority of the experiments were performed by procedures similar to those detailed for 9. Isolated yields are generally reduced from those observed spectroscopically due to the high solubility of the compounds. <sup>1</sup>H and <sup>13</sup>C NMR data are found in Tables I and II, respectively.<sup>18</sup>

( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiCH=C(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub> (3) and ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti(C≡CCH<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>) (4). Toluene (10 mL) and propyne (2.0 mmol) were condensed into a flask containing 1 (700 mg, 2.02 mmol). The solution was warmed to 25 °C and stirred overnight. Volatiles were removed in vacuo, and the red-orange residue was recrystallized from octane to yield an 80:20 mixture of 3 and 4. Samples

left in solution contained no 4 (<sup>1</sup>H NMR) after several days while the concentration of 3 increased proportionally vs. an internal standard. Isolated yield of 3: 450 mg (58%); IR 2725 (w), 1587 (m), 1495 (m), 1312 (w), 1023 (s), 400 (s), cm<sup>-1</sup>. Anal. Calcd for C<sub>25</sub>H<sub>38</sub>Ti: C, 77.70; H, 9.91; Ti, 12.39; mol wt, 386. Found: C, 77.15; H, 9.87; Ti, 12.66; mol wt, 384. 4: IR 2720 (w), 2100 (s), 1115 (m), 1023 (s), 973 (s) cm<sup>-1</sup>. Addition of Me<sub>3</sub>CC≡CH to 1 similarly gives ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti(C≡CCMe<sub>3</sub>)(C<sub>2</sub>H<sub>5</sub>) (5) as determined by NMR.

( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiC(CH<sub>3</sub>)=C(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub> (6). Toluene (5 mL), 2-butyne (8 mmol), and ethylene (2 mmol) were condensed at -196 °C into a flask containing 1 (250 mg, 0.72 mmol). The mixture was warmed to 25 °C and stirred 12 h. Volatiles were removed under vacuum at 0 °C to yield a crude red-orange solid which was recrystallized from petroleum ether: yield (two crops) 200 mg (70%); IR 2795 (w), 2720 (w), 1580 (m), 1492 (m), 1020 (s), 590 (w) cm<sup>-1</sup>. Anal. Calcd for C<sub>26</sub>H<sub>40</sub>Ti: C, 77.97; H, 10.07; Ti, 11.96; mol wt, 401. Found: C, 77.75; H, 9.94; Ti, 11.85; mol wt, 386.

( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiN=C(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub> (9). Toluene-*d*<sub>8</sub> (0.3 mL) and CH<sub>3</sub>CN (0.073 mmol) were condensed at -196 °C into an NMR tube containing 1 (0.069 mmol). The mixture was warmed to -78 °C and the reaction monitored by <sup>1</sup>H and <sup>13</sup>C NMR between -70 and 30 °C.

Petroleum ether (7 mL) and acetonitrile (0.88 mmol) were condensed at -196 °C into a 10-mL flask containing 1 (230 mg, 0.66 mmol). The mixture was warmed to -40 °C, stirred 30 min, and then cooled to -78 °C. The slurry of red-orange crystals was filtered and dried below -30 °C, affording 160 mg of 9 (62%): IR (from sample containing 9 and 10) 3370 (w), 2725 (w), 1638 (s), 1571 (m), 1280 (m), 1148 (m), 1020 (s), 645 (s), 617 (s) 595 (s), 517 (s) cm<sup>-1</sup>. Similar procedures were employed for the isolation

of ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiN=C(C<sub>2</sub>H<sub>5</sub>)CH<sub>2</sub>CH<sub>2</sub> (11), ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiN=C(CMe<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub> (12) and ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiN=C(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub> (13). 11: yield 86%; IR 2722 (w), 1640 (s), 1278 (s), 1100 (s), 1020 (s), 942 (m), 663 (s), 510 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>25</sub>H<sub>39</sub>NTi: C, 74.79; H, 9.79; N, 3.49; Ti, 11.93; mol wt, 401. Found: C, 74.64; H, 9.85; N, 3.31; Ti, 12.05; mol wt, 390. 12: yield 56%; IR 1620 (s), 1283 (w), 1055 (m), 1020 (m), 950 (m), 635 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>27</sub>H<sub>43</sub>NTi: C, 75.50; H, 10.09; N, 3.26; Ti, 11.15. Found: C, 74.84; H, 9.97; N, 3.52; Ti, 11.30. 13: yield 28%; IR 2725 (w), 1680 (s), 1555 (w), 1215 (s), 1022 (s), 830 (s), 455 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>30</sub>H<sub>41</sub>NTi: C, 77.73; H, 8.92; N, 3.02; mol wt, 464. Found: C, 77.64; H, 8.70; N, 3.21; mol wt, 439.

( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiOC(O)CH<sub>2</sub>CH<sub>2</sub> (15). Carbon dioxide (1.07 mmol) was added to a stirred solution of 1 (360 mg, 1.04 mmol) in 10 mL of toluene at -78 °C. The reaction was allowed to proceed 15 min at -78 °C, and then the mixture was warmed to 25 °C. The toluene and excess CO<sub>2</sub> were removed under vacuum, and the resulting red solid was recrystallized from cold petroleum ether to give 325 mg (80%) pure 15. IR 1657 (vs), 1277 (s), 1250 (s), 1219 (m), 1020 (m), 895 (s), 860 (m), 421 (s), 380 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>23</sub>H<sub>34</sub>TiO<sub>2</sub>: C, 70.76; H, 8.78; Ti, 12.27; mol wt, 390. Found: C, 70.31; H, 8.81; Ti, 12.15; mol wt, 386.

( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiOCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub> (16). Following the same procedure as that used for 15, the red-orange, very soluble 16 was isolated in 31% yield: IR 2722 (w), 1363 (m), 1320 (m), 1217 (m), 1115 (m), 1080 (s), 1020 (m), 1002 (m), 903 (s), 830 (m), 582 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>24</sub>H<sub>38</sub>TiO: C, 73.83; H, 9.81; Ti, 12.27. Found: C, 73.40; H, 9.93; Ti, 12.79.

**Carbonylation of 6.** Benzene-*d*<sub>6</sub> (0.5 mL) was condensed at -196 °C into a thick-walled glass vessel containing 6 (45 mg, 0.13 mmol). Carbon monoxide (10 mmol) was added, and the contents were heated and stirred at 80 °C for 48 h. The excess CO was removed by three freeze-pump-thaw cycles at -196 °C; then the benzene-*d*<sub>6</sub> and any volatiles were vacuum transferred at 25 °C into an NMR tube and found to contain a trace of 2,3-dimethylcyclopent-2-enone. The contents of the glass vessel were identified as ( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti(CO)<sub>2</sub> and 2,3-dimethylcyclopent-2-enone by <sup>1</sup>H NMR and IR.<sup>6,7</sup>

**Acknowledgment.** This work has been supported by the National Science Foundation (Grant No. CHE-

(14) Contributions by the Ti<sup>II</sup>( $\eta^4$ -azabutadiene) (19b) or the Ti<sup>IV</sup>( $\sigma^2$ , $\eta$ -metallacyclopent-3-enamine) (19a) resonance structures may impart to the titanacycloenamine 10 a nonplanar ring geometry similar to those found for group 4 metallocene dithiolene<sup>15</sup> and butadiene<sup>16</sup> complexes, thereby providing a plausible rationale for the influence of the imine = enamine equilibrium by steric interactions between the C<sub>5</sub>Me<sub>5</sub> rings and the seemingly remote alkyl or aryl substituent R. In this connection it is noteworthy that a single resonance for the [ $\eta$ -C<sub>5</sub>Me<sub>5</sub>] ligands of 10 is observed even at 0 °C.<sup>15,16</sup>

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8303735). We also acknowledge use of the Southern California Regional NMR Facility and the support of NSF Grant CHE-7916324A1.

**Registry No.** 1, 83314-27-6; 3, 95865-15-9; 4, 95865-16-0; 5, 95865-17-1; 6, 95865-18-2; 7, 95865-19-3; 8, 95865-20-6; 9, 95865-21-7; 9-*d*<sub>3</sub>, 95865-22-8; 9-<sup>13</sup>C<sub>2</sub>, 95865-23-9; 9-<sup>15</sup>N, *d*<sub>4</sub>, 95865-24-0; 10, 95865-25-1; 10-*d*<sub>3</sub>, 95892-03-8; 10-<sup>13</sup>C<sub>2</sub>, 95865-26-2; 10-<sup>15</sup>N, *d*<sub>4</sub>, 95865-27-3; 11, 95865-28-4; 12, 95865-29-5; 13, 95865-30-8; 14, 95865-31-9; 15, 95865-32-0; 16, 95892-04-9; (η-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti(CO)<sub>2</sub>, 11136-40-6; (η-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti(η-CH<sub>3</sub>C≡CCH<sub>2</sub>CH<sub>3</sub>), 95892-05-0; (η-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti(η-CH<sub>3</sub>C≡C(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 95865-33-1; (η-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti(η-CH<sub>3</sub>C≡CPh), 95865-34-2; (η-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiC(CH<sub>3</sub>)=C(CH<sub>2</sub>CH<sub>3</sub>)-CH<sub>2</sub>CH<sub>2</sub>, 95865-35-3; (η-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti(C(CH<sub>2</sub>CH<sub>3</sub>)=C(CH<sub>3</sub>)-CH<sub>2</sub>CH<sub>2</sub>), 95865-36-4; (η-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiC(CH<sub>3</sub>)=C[(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>]-CH<sub>2</sub>CH<sub>2</sub>, 95865-37-5; (η-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiC((CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>)=C(CH<sub>3</sub>)-

CH<sub>2</sub>CH<sub>2</sub>, 95865-38-6; (η-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiC(CH<sub>3</sub>)=C(Ph)CH<sub>2</sub>CH<sub>2</sub>, 95865-39-7; (η-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiC(Ph)=C(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>, 95892-06-1; (η-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiO(CH<sub>3</sub>)<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>, 95865-40-0; [(η-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti](μ-N<sub>2</sub>), 11136-46-2; CO<sub>2</sub>, 124-38-9; CO, 630-08-0; Me<sub>3</sub>CC≡CH, 917-92-0; CH<sub>3</sub>CN, 75-05-8; CD<sub>3</sub>CN, 2206-26-0; <sup>13</sup>CH<sub>2</sub><sup>13</sup>CH<sub>2</sub>, 51915-19-6; propyne, 74-99-7; 2-butyne, 503-17-3; ethylene, 74-85-1; allene, 463-49-0; diphenylacetylene, 501-65-5; 2-pentyne, 627-21-4; 2-octyne, 2809-67-8; 1-phenylpropyne, 673-32-5; propionitrile, 107-12-0; 2,2-dimethylpropionitrile, 630-18-2; *p*-tolunitrile, 104-85-8; acetaldehyde, 75-07-0; acetone, 67-64-1; 2,3-dimethylcyclopent-2-enone, 1121-05-7.

**Supplementary Material Available:** Spectroscopic data for (η-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti(η-CH<sub>3</sub>C≡CR) and the corresponding isomeric metallacyclopentenes, where R = C<sub>2</sub>H<sub>5</sub>, CH<sub>2</sub>(CH<sub>2</sub>)CH<sub>3</sub>, and Ph (2 pages). Ordering information is given any current masthead page.

## Effects of the Conformational Rearrangement of the (np<sub>3</sub>)M Fragment in the Course of the Reaction between (np<sub>3</sub>)MH Hydrides [M = Co, Rh; np<sub>3</sub> = N(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>] and Carbon Disulfide

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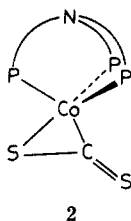
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Received June 25, 1984

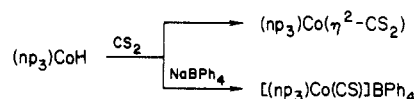
The reactivity of the complex (np<sub>3</sub>)RhH toward CS<sub>2</sub> has been investigated. Depending on the presence or absence of NaBPh<sub>4</sub> in the reaction mixture, two different compounds are obtained: [(np<sub>3</sub>)Rh(η<sup>2</sup>-CS<sub>2</sub>)]BPh<sub>4</sub>·0.5C<sub>2</sub>H<sub>5</sub>OH and (np<sub>3</sub>)Rh(S<sub>2</sub>CH). In contrast to the rhodium hydride, the cobalt analogue is reported to yield [(np<sub>3</sub>)Co(CS)]BPh<sub>4</sub> and (np<sub>3</sub>)Co(η<sup>2</sup>-CS<sub>2</sub>). An indirect way of obtaining a stable rhodium analogue of the cobalt thiocarbonyl complex is presented. The structure of the Rh(I)-η<sup>2</sup>-CS<sub>2</sub> complex has been determined by X-ray diffraction analysis in order to compare its stereochemical features with those of the Co(0) analogue: *a* = 19.134 (3) Å, *b* = 17.061 (3) Å, *c* = 9.111 (1) Å, α = 83.95 (2)°, β = 79.70 (1)°, γ = 84.46 (1)°, triclinic, *P*1̄, *Z* = 2. In the complex cation the (np<sub>3</sub>)M fragment distorts from the common C<sub>3v</sub> symmetry by accommodating two phosphorus atoms in trans axial positions of an octahedron; the nitrogen and the third phosphorus atoms lie cis to each other in the equatorial plane. This arrangement corresponds to the shape of typical L<sub>4</sub>M fragments with C<sub>2v</sub> symmetry where d<sup>8</sup> metal fragments of this type are supportive of η<sup>2</sup>-CS<sub>2</sub> coordination. Although the four different products obtainable from the reaction of the cobalt and rhodium hydrides with CS<sub>2</sub> indicate multiple-reaction pathways, there is enough evidence that these may be caused by the ease of the rearrangement of the (np<sub>3</sub>)M fragment and by the amphoteric nature of the (np<sub>3</sub>)MH hydrides. This paper, by referring to a series of experimental and theoretical observations for complexes containing the (np<sub>3</sub>)M fragment, offers suggestions as to how one can interpret major, different trends of the reactivity. Qualitative MO arguments, supported in some cases by EHMO calculations, are used to check whether the existence of the proposed key intermediates is allowed or not.

### Introduction

In a recent paper we described CS<sub>2</sub> chemistry of a reactive metal hydride, namely, the complex (np<sub>3</sub>)CoH, 1 [np<sub>3</sub> = tris(2-(diphenylphosphino)ethyl)amine].<sup>1</sup> Depending on the presence of NaBPh<sub>4</sub> in the reaction mixture, two different products can be obtained: (i) a para-



### Scheme I



magnetic cobalt(0) complex, (np<sub>3</sub>)Co(η<sup>2</sup>-CS<sub>2</sub>), which was assigned the structure 2; (ii) a cobalt(I) thiocarbonyl complex, [(np<sub>3</sub>)Co(CS)]BPh<sub>4</sub>, 3, as shown in Scheme I.

The unique bonding capabilities of the ligand np<sub>3</sub> must play an important role in determining the different reactivities of (np<sub>3</sub>)CoH. In effect, the ligand envelopes the metal in different modes that ultimately affect the mobility of hydrogen over the coordination sphere and hence the different modes of rupture of the M-H linkage.<sup>2,3</sup> This

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