Journal of Organometallic Chemistry, 476 (1994) 197–206

Novel acetylene complexes of titanocene and permethyltitanocene without additional ligands. Synthesis, spectral characteristics and X-ray diffraction study

V.V. Burlakov, A.V. Polyakov, A.I. Yanovsky, Yu.T. Struchkov, V.B. Shur and M.E. Vol'pin

A.N. Nesmeyanov Institute of Organo-Element Compounds of the Russian Academy of Sciences, Vavilov St. 28, Moscow 117813 (Russian Federation)

U. Rosenthal

Max-Planck-Gesellschaft, Arbeitsgruppe 'Komplexkatalyse' an der Universität Rostock, Buchbinderstrasse 5–6, D-18055 Rostock (Germany)

H. Görls

Max-Planck-Gesellschaft, Arbeitsgruppe 'CO_2-Chemie' an der Universität Jena, Lessingstrasse 12, D-07743 Jena (Germany)

(Received November 8, 1993)

Abstract

New acetylene complexes of titanocene and permethyltitanocene $Cp_2Ti(R^1C_2R^2)$ and $Cp^*_2Ti(R^1C_2R^2)$ ($R^1 = R^2 = SiMe_3$; $R^1 = Ph$, $R^2 = SiMe_3$) without additional ligands have been prepared by the reaction of Cp_2TiCl_2 and $Cp^*_2TiCl_2$ with equimolar amounts of Mg and the appropriate acetylene $R^1C_2R^2$ in THF. The complexes have been isolated from the reaction mixture in an analytically pure state and characterized by spectral methods. The structures of complexes $Cp_2Ti(PhC_2SiMe_3)$, $Cp^*_2Ti(PhC_2SiMe_3)$ and $Cp^*_2Ti(Me_3SiC_2SiMe_3)$ have been proved by an X-ray diffraction study. Some chemical properties of the synthesized complexes have been investigated.

Key words: Titanium; X-ray diffraction; Infrared spectroscopy; Nuclear magnetic resonance; Crystal structure

1. Introduction

Titanium compounds exhibit high catalytic activity in various transformations of acetylenes such as polymerization, oligomerization, hydrogenation, cyclization, *etc*. It is generally believed that a key step in these reactions is the formation of intermediate acetylene titanium complexes in which the acetylene hydrocarbon molecule is activated towards further transformations. Hence, it is not surprising that attempts have been made in various laboratories to obtain such acetylene complexes in order to study their structure, reactivity and catalytic activity. However, such attempts were unsuccessful for a long time (see, for example, refs. 1 and 2).

The first acetylene complex of titanium, $Cp_2Ti(PhC_2Ph)(CO)$, was obtained by Fachinetti and Floriani in 1974 [3]. The complex is a titanocene derivative and contains coordinated tolane and carbon monoxide molecules. The structure of the complex was established by an X-ray diffraction study. In further studies of other workers, similar acetylene complexes $Cp_2Ti(C_6F_5C_2C_6F_5)(CO)$ and $Cp_2Ti(R^1C_2R^2)(PR_3)$, containing coordinated CO or phosphine molecules as additional ligands, were described [4–6].

In 1982 we reported the synthesis of the first acetylene complex of titanocene, $Cp_2Ti(PhC_2Ph)$ (I), containing no additional carbonyl nor phosphine ligands. The complex was isolated in an analytically pure state from a mixture and characterized [7,8]. Analogous acetylene complexes of permethyltitanocene, $Cp^*_2Ti(PhC_2Ph)$ and $Cp^*_2Ti(MeC_2Me)$, and of pentamethyltitanocene, $Cp^*CpTi(PhC_2Ph)$, were prepared by

---

Correspondence to: Professor V.B. Shur.

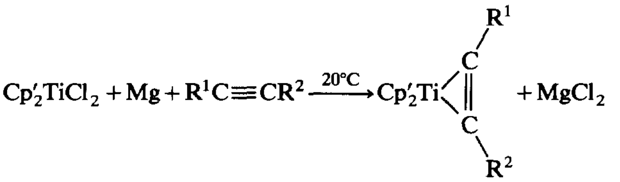
Elsevier Science S.A.

Bercaw *et al.* [9] and Dixneuf *et al.* [10], respectively. Their structures were determined by spectral and chemical means but X-ray diffraction studies of these complexes were not carried out as in the case of complex **I**.

In the present paper we report the synthesis, spectral characteristics and some chemical properties of a number of new acetylene complexes of titanocene and permethyltitanocene containing no additional ligands, as well as the results of the first X-ray diffraction studies of such complexes. For preliminary communications, see refs. 11–13.

2. Results and discussion

The first acetylene complex of titanocene **I** without additional ligands was prepared by the interaction of Cp_2TiCl_2 with equimolar amounts of magnesium and tolane in THF at room temperature [7,8]. We have found that this procedure can be used successfully for the synthesis of complexes of titanocene and permethyltitanocene with phenyl(trimethylsilyl)- and bis(trimethylsilyl)-acetylenes (**II**–**V**). The reaction proceeds at room temperature for 2.5–4.5 h. The yield of pure complex is 50–75%.



$$Cp'_2TiCl_2 + Mg + R^1C{\equiv}CR^2 \xrightarrow{20^{\circ}C} Cp'_2Ti(C(R^1){=}C(R^2)) + MgCl_2$$

$Cp' = Cp = \eta^5\text{-}C_5H_5$ $R^1 = R^2 = Ph$ (**I**)
$R^1 = R^2 = SiMe_3$ (**II**)
$R^1 = Ph$; $R^2 = SiMe_3$ (**III**)
$Cp' = Cp^* = \eta^5\text{-}C_5Me_5$ $R^1 = R^2 = SiMe_3$ (**IV**)
$R^1 = Ph$, $R^2 = SiMe_3$ (**V**)

All four complexes **II**–**V** were isolated from the respective reaction mixture as definite compounds and characterized by analytical and spectral methods. The structure of complexes **III**–**V** was also confirmed by X-ray diffraction studies (see below).

Complexes **II**–**V** are coloured crystalline substances readily soluble in ethereal and hydrocarbon solvents. In the solid state the complexes are stable under Ar at room temperature, but they rapidly decompose in the presence of air or moisture.

IR spectra of **II**, **III** and **V** within the range of 1550–2300 cm^{-1} exhibit a single absorption band at 1625–1687 cm^{-1} (Table 1) that can be assigned to stretching vibrations of the coordinated C≡C bond of the acetylene group. The IR spectrum of **IV** displays two bands (at 1598 and 1563 cm^{-1}) in this region. Such low values of $\nu(C{\equiv}C)$ in the spectra of **II**–**V** indicate that the synthesized complexes as well as complex **I** ($\nu(C{\equiv}C) = 1713$ cm^{-1} [8]) have a structure close to that of titanacyclopene.

Table 1 presents data on the $\nu(C{\equiv}C)$ frequencies for all presently known acetylene complexes of titanocene and permethyltitanocene of the types $Cp_2Ti(R^1C_2R^2)$ and $Cp^*_2Ti(R^1C_2R^2)$. Differences $\Delta\nu(C{\equiv}C)$ between the $\nu(C{\equiv}C)$ values for the free and coordinated acetylene molecules are also listed in this table. As can be seen from Table 1, on passing from complexes with $\eta^5\text{-}C_5H_5$ ligands to complexes with more electron-donating $\eta^5\text{-}C_5Me_5$ ligands, the value of $\nu(C{\equiv}C)$ decreases while that of $\Delta\nu(C{\equiv}C)$ increases. These changes are obviously caused by the increasing efficiency of electron transfer from the titanium atom to the acetylene ligand.

The ^1H NMR spectra of **II** and **III** exhibit singlets corresponding to the η^5-cyclopentadienyl protons (δ 6.45 and 6.31 ppm, respectively), while those of **IV** and **V** display singlets corresponding to the methyl protons of the $\eta^5\text{-}C_5Me_5$ rings (δ 1.72 and 1.75 ppm, respectively). The ^1H NMR spectra of **III** and **V** show multiplets corresponding to the phenyl protons (δ 6.18–7.04 and 6.12–6.91 ppm, respectively). The spectra of all the complexes **II**–**V** also contain singlets of protons corresponding to the $SiMe_3$ groups (δ from −0.29 to +0.02

TABLE 1. Frequencies $\nu(C{\equiv}C)$ (cm^{-1}) in the IR spectra of acetylene complexes of titanocene $Cp_2Ti(R^1C_2R^2)$ and permethyltitanocene $Cp^*_2Ti(R^1C_2R^2)$

R^1 and R^2 in acetylene	$\nu(C{\equiv}C)$ for free acetylene	$Cp_2Ti(R^1C_2R^2)$		$Cp^*_2Ti(R^1C_2R^2)$	
		$\nu(C{\equiv}C)$	$\Delta\nu(C{\equiv}C)$	$\nu(C{\equiv}C)$	$\Delta\nu(C{\equiv}C)$
$R^1 = R^2 = SiMe_3$	2107	1687	420	1598, 1563	527
$R^1 = R^2 = Me$	2233	–	–	1683 [a]	550
$R^1 = SiMe_3$, $R^2 = Ph$	2160	1686	474	1625	535
$R^1 = R^2 = Ph$	2223	1713 [b]	510	1647 [a]	576

[a] Ref. 9. [b] Ref. 8.

TABLE 2. Chemical shifts $\delta(C\equiv C)$ (ppm) in the $^{13}C\{^1H\}$ NMR spectra of acetylene complexes of titanocene $Cp_2Ti(R^1C_2R^2)$ and permethyltitanocene $Cp^*_2Ti(R^1C_2R^2)$

R^1 and R^2 in acetylene	$\delta(C\equiv C)$ for free acetylene	$Cp_2Ti(R^1C_2R^2)$		$Cp^*_2Ti(R^1C_2R^2)$	
		$\delta(C\equiv C)$	$\Delta\delta(C\equiv C)$	$\delta(C\equiv C)$	$\Delta\delta(C\equiv C)$
$R^1 = R^2 = SiMe_3$	114.0	244.7	130.9	248.5	134.5
$R^1 = R^2 = Me$	74.3	–	–	200.1 [a]	125.7
$R^1 = SiMe_3$, $R^2 = Ph$	92.5	213.0	120.5	213.2	120.7
	104.4	219.6	115.2	224.9	120.5
$R^1 = R^2 = Ph$	90.1	196.5 [b]	106.4	200.9 [a]	110.8

[a] Ref. 9. [b] Ref. 8.

ppm). In all cases, the ^1H NMR signal intensity ratios are close to the theoretical values.

The $^{13}C\{^1H\}$ NMR spectra of **II** and **IV** show, in addition to other signals (see Experimental details), characteristic singlets of acetylene carbon atoms with $\delta(C\equiv C)$ 244.9 and 248.5 ppm, respectively. The carbon atoms of the acetylene group in complexes **III** and **V** are not equivalent, so the $^{13}C\{^1H\}$ NMR spectra of **III** and **V** exhibit two singlets for the acetylene C atoms with $\delta(C\equiv C)$ 213.0 and 219.6 ppm and $\delta(C\equiv C)$ 213.2 and 224.9 ppm, respectively. As in the free acetylenes, the downfield singlet is produced by the carbon atom bonded to the Ph group, while the upfield singlet is caused by the carbon atom bonded to the $SiMe_3$ group.

Values of $\Delta\delta(C\equiv C)$ for complexes **II–V** representing differences in the chemical shifts $\delta(C\equiv C)$ between coordinated and free acetylenes are of the order of 115.2–134.5 ppm (Table 2). Other known acetylene complexes of titanocene or permethyltitanocene of similar type are characterized by $\delta(C\equiv C)$ and $\Delta\delta(C\equiv C)$ values ranging from 196.5 to 200.9 ppm and from 106.4 to 125.7 ppm, respectively (Table 2). The observed ranges of $\delta(C\equiv C)$ and $\Delta\delta(C\equiv C)$ values for complexes $Cp_2Ti(R^1C_2R^2)$ and $Cp^*_2Ti(R^1C_2R^2)$ indicate that the coordinated acetylene molecule in all such complexes (including **II–V**) is a four-electron ligand (see refs. 8, 14–16).

An X-ray diffraction study of **III–V** showed that the coordination environment of the titanium atom in the complexes is indeed formed by two η^5-cyclopentadienyl rings (permethylated in the case of **IV** and **V**) and a substituted acetylene ligand (Figs. 1–3).

Complexes **III–V** possess the wedge-shaped sandwich structure typical for bis(cyclopentadienyl)titanium derivatives. The coordinated acetylene ligand in the complexes is located in the bisector plane and forms nearly equal dihedral angles (20–22°) with each of the cyclopentadienyl ligand planes (Table 3), the values of these angles (as well as those of the dihedral angles between the Cp or Cp* ligands themselves) being almost identical, notwithstanding the different degree of substitution of the Cp rings.

The carbon atoms of the acetylene, together with the Si and C atoms bonded to them, form almost a planar system in all cases: the torsion angles SiC≡CC

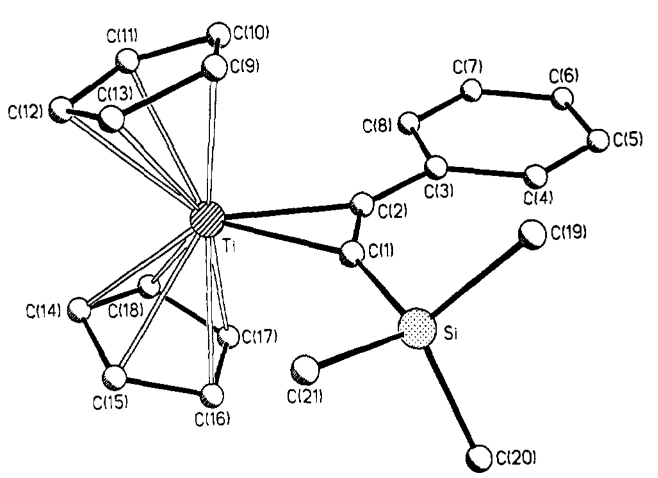


Fig. 1. Structure of complex **III**.

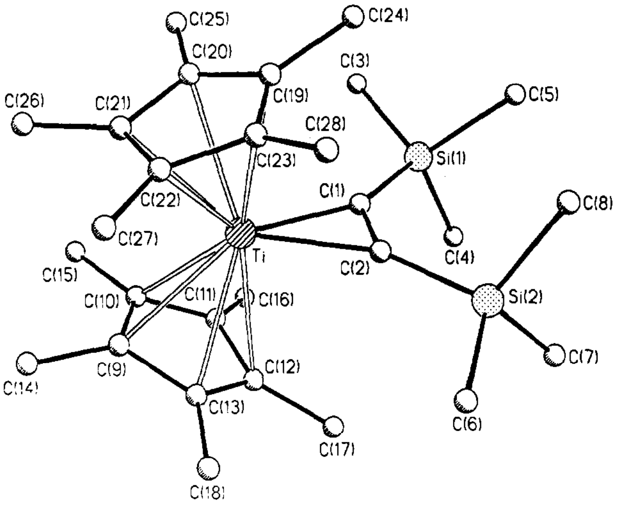


Fig. 2. Structure of complex **IV**.

TABLE 3. Some of the most important angles (°) in the molecules **III**–**V**

Complex	Dihedral angle between the planes of the Cp or Cp* ligands	Dihedral angle (av.) between the planes of the Cp or Cp* ligand and TiC_2	Bond angles	
			C(2)–C(1)–R	C(1)–C(2)–R
IIIA	42.3	21.2	148.2(2)	140.8(3)
IIIB	44.8	22.5	151.9(2)	141.0(3)
IV	41.1	20.6	134.8(3)	136.8(3)
V	40.6	20.4	140.5(2)	138.1(2)

are 3.9 and 2.8° in the two independent molecules **A** and **B** of **III** and −6.5° in **V**; the SiC≡CSi angle in **IV** is −0.2°. Both electronic and steric intramolecular effects in **III** and **V** obviously allow some freedom of rotation of the plane of the phenyl ring around the C–Ph σ-bond. It is of interest, however, that the plane of the benzene ring in the sterically more hindered complex **V** (containing permethylated Cp* rings) forms a larger dihedral angle with the TiC_2 plane (22.2°) than that in the considerably less overcrowded molecule of **III** (2.1° in **IIIA** and 5.1° in **IIIB**). Hence, it may be assumed that a certain value of this parameter within a particular interval around zero is determined by molecular packing in the crystal.

The intramolecular steric effects also determine the mutual arrangement of the η^5-C_5Me_5 ligands in **IV** and **V**, where the Cp* rings have a staggered conformation as in other permethylated bis(cyclopentadienyl) complexes. At the same time, in both independent molecules of **III**, the bis(cyclopentadienyl)titanium unit (with unsubstituted Cp ligands) has an almost eclipsed conformation. The carbon atoms of the methyl substituents in the cyclopentadienyl ligands of complexes **IV** and **V** are displaced from the planes of the C_5 rings in the direction opposite to the metal atom by 0.040–0.390 and 0.053–0.394 Å, respectively, the values on the upper limits of these ranges also being obviously influenced by steric hindrance. It is noteworthy that the most significant deviations from the Cp* ring planes are observed for those methyl groups which are most remote from the acetylene ligand.

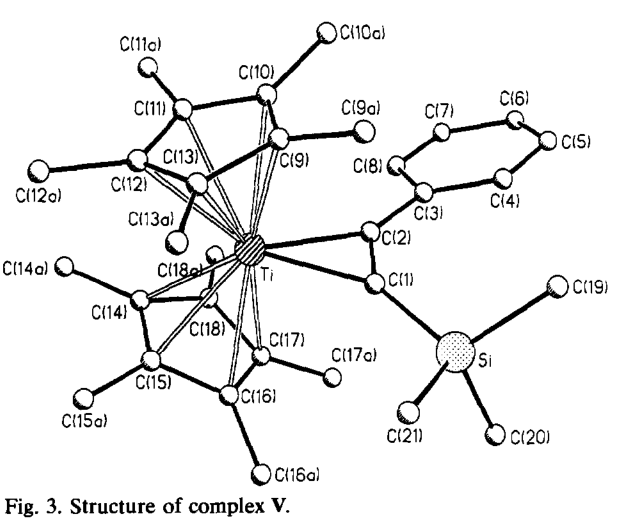
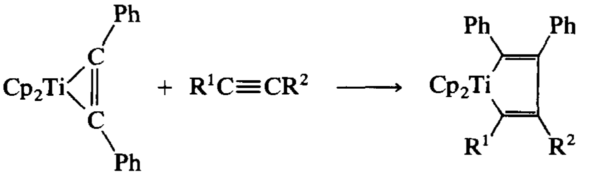


Fig. 3. Structure of complex **V**.

One of the most important features of complexes **III**–**V** is that the coordinated C≡C bond in the acetylene ligand (1.289(4) Å in **IIIA**, 1.279(4) Å in **IIIB**, 1.309(4) Å in **IV** and 1.308(3) Å in **V**, Tables 4–6) is in all cases considerably longer than the normal triple C≡C bond (1.181 Å), its length being close to the value of 1.331 Å typical of the C=C double bond [17]. On passing from **III** to **IV** and **V**, the C≡C distance in the acetylene group increases somewhat as a result of the higher electron-donating capacity of the η^5-C_5Me_5 ligands relative to that of the unsubstituted η^5-C_5H_5 ligands. The distances between the titanium atom and the carbon atoms in the acetylene ligand in **III**–**V** span the range 2.092(3)–2.139(3) Å, which is close to the length of endocyclic Ti–C(sp^2) σ-bond (2.13–2.22 Å [18]). Coordination of acetylene with the titanium atom in **III**–**V** results in a considerable decrease in the corresponding SiCC and CCC bond angles (134.8(3)–151.9(2)°) which are much smaller than 180° and approach the value of 120° typical of the sp^2-hybridized carbon atom. Thus, complexes **III**–**V** have a structure close to that of titanacyclopropene.

Although complexes **I**–**V** have a similar structure, they differ from each other in their reactivity. Earlier, it was shown that the interaction of the tolane complex of titanocene **I** with tolane and some other acetylenes at 20°C results in the insertion of an acetylene molecule into the Ti–C bond of the titanacyclopropene ring of **I** yielding titanacyclopentadiene metallacycles [8,19,20]:



(**I**)

A different picture was observed in the reaction of acetylenes with the bis(trimethylsilyl)acetylene complex

TABLE 4. Bond lengths (Å) in the two independent molecules (**A** and **B**) of **III**

	Molecule			Molecule	
	A	**B**		**A**	**B**
Ti–C(1)	2.118(3)	2.112(3)	C(2)–C(3)	1.457(4)	1.471(4)
Ti–C(2)	2.095(3)	2.092(3)	C(3)–C(4)	1.394(4)	1.393(4)
Ti–C(9)	2.394(3)	2.414(4)	C(3)–C(8)	1.393(4)	1.390(4)
Ti–C(10)	2.369(3)	2.344(4)	C(4)–C(5)	1.389(4)	1.391(5)
Ti–C(11)	2.377(3)	2.320(4)	C(5)–C(6)	1.384(5)	1.387(6)
Ti–C(12)	2.408(3)	2.373(4)	C(6)–C(7)	1.374(5)	1.371(5)
Ti–C(13)	2.404(3)	2.404(4)	C(7)–C(8)	1.396(4)	1.401(5)
Ti–C(14)	2.388(4)	2.394(4)	C(9)–C(10)	1.391(5)	1.381(6)
Ti–C(15)	2.378(4)	2.414(3)	C(9)–C(13)	1.417(5)	1.329(5)
Ti–C(16)	2.376(4)	2.408(3)	C(10)–C(11)	1.406(5)	1.431(6)
Ti–C(17)	2.371(3)	2.359(3)	C(11)–C(12)	1.386(5)	1.376(5)
Ti–C(18)	2.371(4)	2.358(3)	C(12)–C(13)	1.397(5)	1.322(6)
Si–C(1)	1.835(3)	1.833(3)	C(14)–C(15)	1.353(6)	1.383(5)
Si–C(19)	1.863(4)	1.826(5)	C(14)–C(18)	1.355(5)	1.405(5)
Si–C(20)	1.867(4)	1.846(4)	C(15)–C(16)	1.385(5)	1.397(5)
Si–C(21)	1.871(4)	1.841(4)	C(16)–C(17)	1.390(5)	1.395(5)
C(1)–C(2)	1.289(4)	1.279(4)	C(17)–C(18)	1.370(5)	1.401(5)

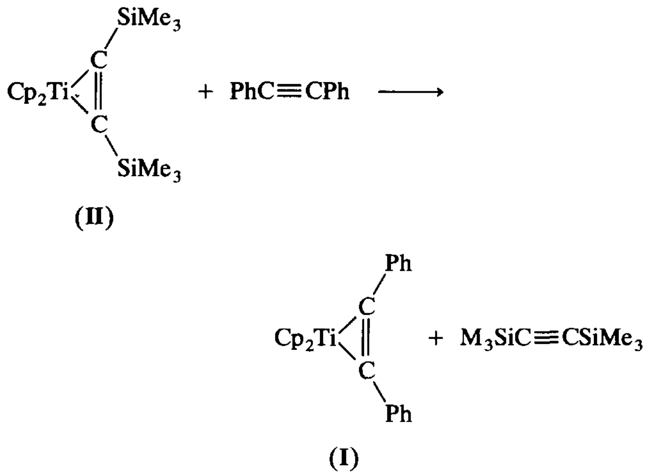
of titanocene **II**. It appears that the interaction of tolane with this complex leads to the gradual displacement of the bis(trimethylsilyl)acetylene ligand from the coordination sphere of titanium. This results in the formation of the intermediate tolane complex of titanocene (**I**) which reacts further with free unreacted tolane to give the corresponding titanacyclopentadiene derivative (**VI**)

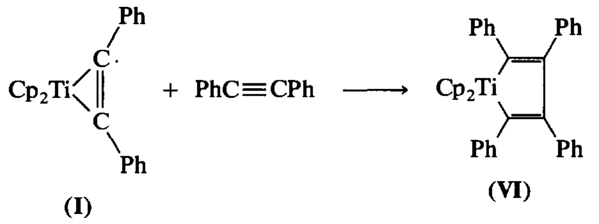
TABLE 5. Bond lengths (Å) in molecule **IV**

Ti–C(1)	2.122(3)	C(9)–C(10)	1.412(4)
Ti–C(2)	2.126(3)	C(9)–C(13)	1.414(4)
Ti–C(9)	2.462(4)	C(9)–C(14)	1.507(5)
Ti–C(10)	2.420(4)	C(10)–C(11)	1.414(5)
Ti–C(11)	2.413(4)	C(10)–C(15)	1.513(5)
Ti–C(12)	2.451(3)	C(11)–C(12)	1.417(4)
Ti–C(13)	2.429(4)	C(11)–C(16)	1.503(5)
Ti–C(19)	2.445(4)	C(12)–C(13)	1.411(4)
Ti–C(20)	2.427(4)	C(12)–C(17)	1.491(5)
Ti–C(21)	2.446(3)	C(13)–C(18)	1.503(4)
Ti–C(22)	2.412(3)	C(19)–C(20)	1.411(5)
Ti–C(23)	2.408(4)	C(19)–C(23)	1.411(5)
Si(1)–C(1)	1.862(3)	C(19)–C(24)	1.498(6)
Si(1)–C(3)	1.869(4)	C(20)–C(21)	1.417(5)
Si(1)–C(4)	1.870(4)	C(20)–C(25)	1.497(5)
Si(1)–C(5)	1.876(5)	C(21)–C(22)	1.418(4)
Si(2)–C(2)	1.856(3)	C(21)–C(26)	1.498(5)
Si(2)–C(6)	1.871(4)	C(22)–C(23)	1.413(5)
Si(2)–C(7)	1.870(4)	C(22)–C(27)	1.506(5)
Si(2)–C(8)	1.878(5)	C(23)–C(28)	1.502(5)
C(1)–C(2)	1.309(4)		

TABLE 6. Bond lengths (Å) in molecule V

Ti–C(1)	2.139(2)	Ti–C(2)	2.089(2)
Ti–C(9)	2.431(2)	Ti–C(10)	2.089(2)
Ti–C(11)	2.418(2)	Ti–C(12)	2.468(2)
Ti–C(13)	2.426(2)	Ti–C(14)	2.457(2)
Ti–C(15)	2.406(2)	Ti–C(16)	2.413(2)
Ti–C(17)	2.479(2)	Ti–C(18)	2.464(2)
Si–C(1)	1.853(2)	Si–C(19)	1.890(3)
Si–C(20)	1.875(3)	Si–C(21)	1.875(3)
C(1)–C(2)	1.308(3)	C(2)–C(3)	1.472(3)
C(3)–C(4)	1.393(3)	C(3)–C(8)	1.390(3)
C(4)–C(5)	1.396(3)	C(5)–C(6)	1.357(4)
C(6)–C(7)	1.384(4)	C(7)–C(8)	1.377(4)
C(9a)–C(9)	1.504(3)	C(9)–C(10)	1.406(3)
C(9)–C(13)	1.415(3)	C(10a)–C(10)	1.506(3)
C(10)–C(11)	1.424(3)	C(11)–C(11a)	1.504(3)
C(11)–C(12)	1.421(3)	C(12a)–C(12)	1.508(3)
C(12)–C(13)	1.410(3)	C(13)–C(13a)	1.502(3)
C(14)–C(14a)	1.508(3)	C(14)–C(15)	1.423(3)
C(14)–C(18)	1.423(3)	C(15a)–C(15)	1.496(3)
C(15)–(16)	1.427(3)	C(16)–C(16a)	1.502(3)
C(16)–C(17)	1.408(3)	C(17)–C(17a)	1.505(3)
C(17)–C(18)	1.412(3)	C(18)–C(18a)	1.496(3)



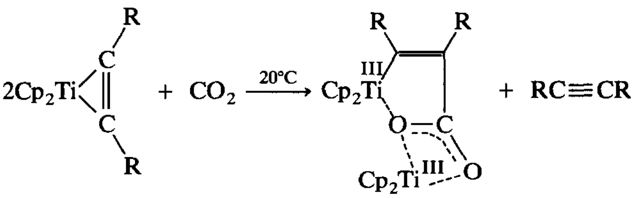


According to ^1H NMR data, even 10 min after mixing **II** ($[II]_0 = 0.10$ M) with an equimolar amount of tolane in C_6D_6 at 20°C, complexes **I** and **VI** as well as free bis(trimethylsilyl)acetylene had appeared in the solution. With time the concentration of **II** in the mixture decreased while that of **I**, **VI** and $Me_3SiC≡CSiMe_3$ increased. After 20 min, the yields of **I** and **VI** were 18% and 4% (per initial complex **II**), respectively, and after 4.5 h they reached values of 47% and 32%, respectively.

Doubling the amount of excess tolane (but keeping the initial concentration of **II** unchanged) increased the reaction rate. Under these conditions, the yields of **I** and **VI** present after 10 min attained values of 26% and 6%, respectively. After 2.5 h, the amount of **I** decreased to 20% and that of **VI** increased to 77%. By this time the reaction mixture only contained traces of the initial **II** and, correspondingly, nearly 100% of free bis(trimethylsilyl)acetylene. Further changes in the ^1H NMR spectrum of the mixture arose from the reaction of the intermediate complex **I** with tolane leading to the formation of **VI**. This process is fully completed within the next few hours. A similar displacement reaction of the bis(trimethylsilyl)acetylene ligand has been observed in the interaction of **II** with 3-hexyne.

Such substitution reactions seem to be quite typical for complex **II**. Indeed, as our preliminary experiments have shown, reactions of this complex with acetone and benzophenone in C_6D_6 at room temperature are also accompanied by a displacement of the acetylene ligand. In contrast to **II**, complex **I** readily adds carbonyl compounds to form titanadihydrofuran metallacycles [18,21]. It is probable that the bulky $SiMe_3$ groups of the coordinated bis(trimethylsilyl)acetylene molecule hinder addition of another acetylene molecule or of a carbonyl compound. As a result, displacement of the acetylene ligand becomes more favourable in this case. It should be noted that the bis(trimethylsilyl)acetylene complex of permethyltitanocene **IV** does not react at all with tolane, evidently also due to steric hindrance.

Although complexes **I** and **II** react with acetylenes and carbonyl compounds in different ways, they behave in the same manner in their reaction with the relatively small-sized CO_2 molecule. As we reported briefly earlier [22], 0.5 mol of free acetylene is released during the interaction of these complexes with carbon dioxide, and binuclear σ-vinylcarboxylate derivatives of trivalent titanium, *i.e.* **VII** and **VIII** containing two fused chelate cycles and a tricoordinated oxygen atom, are formed.



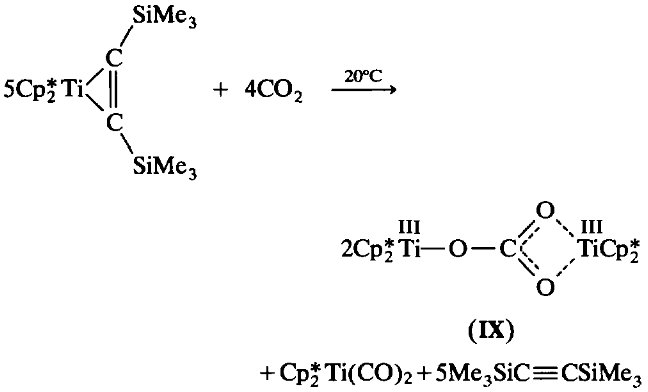
R = Ph (**VII**)
R = $SiMe_3$ (**VIII**)

It is of interest, however, that the reaction of carbon dioxide with the bis(trimethylsilyl)acetylene complex of permethyltitanocene **IV** occurs in quite a different manner. In this case, full displacement of bis(trimethyl-

TABLE 7. Crystal data and parameters from X-ray structural studies of complexes **III**–**V**

	Complex **III**	Complex **IV**	Complex **V**
System	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.727(6)	8.955(2)	9.651(2)
b (Å)	12.987(5)	10.077(2)	10.360(2)
c (Å)	13.935(4)	17.263(3)	15.665(3)
α (°)	95.06(3)	79.50(2)	84.44(1)
β (°)	112.79(2)	76.04(2)	72.71(1)
γ (°)	94.72(3)	73.31(2)	72.35(1)
V (Å^3)	1933(1)	1437.3(3)	1425.1(1)
Z	4	2	2
$d_{calc.}$ (g cm^{-3})	1.21	1.13	1.15
Number of unique reflections with $I \geq 3\sigma(I)$	7886	3556	6717
R	0.061	0.038	0.051
R_w	0.059	0.057	0.051

silyl)acetylene from the titanium coordination sphere takes place and carbon dioxide undergoes disproportionation to give $Cp^*_2Ti(CO)_2$ and the binuclear carbonato complex of permethyltitanocene $(Cp^*_2Ti)_2CO_3$ (**IX**) [23].



The reactions of **I**, **II** and **IV** with carbon dioxide will be described in greater detail in subsequent publications.

3. Experimental details

Experiments were conducted under Ar with careful exclusion of air and moisture. Solvents were purified by conventional methods and distilled before use over sodium and sodium benzophenoneketyl (THF) or over

TABLE 8. Atomic coordinates in complex **III**

Atom	Molecule **A**			Molecule **B**		
	x	y	z	x	y	z
Ti	0.1318(1)	0.2497(1)	0.2895(1)	0.5311(1)	0.2730(1)	−0.1973(1)
Si	0.1068(1)	0.2359(1)	0.0140(1)	0.4124(1)	−0.0054(1)	−0.2597(1)
C(1)	0.1789(2)	0.2579(2)	0.1580(2)	0.4036(2)	0.1351(2)	−0.2523(2)
C(2)	0.2775(2)	0.2876(2)	0.2423(2)	0.3420(2)	0.2133(2)	−0.2670(2)
C(3)	0.4101(2)	0.3223(2)	0.2764(2)	0.2133(2)	0.2385(2)	−0.3046(2)
C(4)	0.4658(2)	0.3329(2)	0.2052(2)	0.1126(3)	0.1600(2)	−0.3388(2)
C(5)	0.5928(3)	0.3644(2)	0.2391(3)	−0.0090(3)	0.1837(3)	−0.3701(3)
C(6)	0.6665(3)	0.3863(2)	0.3454(3)	−0.0309(3)	0.2870(3)	−0.3695(3)
C(7)	0.6136(3)	0.3766(3)	0.4171(2)	0.0667(3)	0.3653(3)	−0.3382(3)
C(8)	0.4859(3)	0.3453(2)	0.3830(2)	0.1894(3)	0.3415(2)	−0.3052(2)
C(9)	0.1564(3)	0.0706(2)	0.2569(2)	0.5325(3)	0.2398(3)	−0.3700(3)
C(10)	0.2481(3)	0.1119(2)	0.3543(3)	0.5001(3)	0.3381(3)	−0.3559(3)
C(11)	0.1889(3)	0.1377(3)	0.4220(2)	0.6074(4)	0.3974(3)	−0.2745(3)
C(12)	0.0615(3)	0.1120(3)	0.3662(3)	0.6967(3)	0.3308(3)	−0.2450(3)
C(13)	0.0388(3)	0.0720(2)	0.2631(3)	0.6489(3)	0.2389(3)	−0.3019(3)
C(14)	0.0115(3)	0.3381(3)	0.3670(3)	0.6796(3)	0.3537(3)	−0.0291(3)
C(15)	−0.0412(3)	0.3439(3)	0.2628(3)	0.6472(3)	0.2527(3)	−0.0159(2)
C(16)	0.0430(4)	0.4039(3)	0.2367(3)	0.5211(3)	0.2404(3)	−0.0332(2)
C(17)	0.1490(3)	0.4332(2)	0.3285(3)	0.4741(3)	0.3338(3)	−0.0596(2)
C(18)	0.1278(3)	0.3911(3)	0.4076(3)	0.5726(3)	0.4048(3)	−0.0563(2)
C(19)	0.1929(3)	0.1512(3)	−0.0416(2)	0.3733(4)	−0.0617(3)	−0.3950(3)
C(20)	0.1020(4)	0.3652(3)	−0.0370(3)	0.3096(4)	−0.0735(3)	−0.2068(4)
C(21)	−0.0551(3)	0.1680(3)	−0.0285(3)	0.5724(3)	−0.0273(3)	−0.1778(3)

sodium and calcium hydride (hexane, pentane and benzene) under Ar. IR spectra were measured on Specord M 80 and Nicolet 7199 FT-IR spectrometers using Apiezon grease M, Nujol or KBr pellets. NMR spectra were recorded on Bruker WP-200-SY and WH-400-FT spectrometers using TMS or cyclohexane (δ 1.42 ppm) as internal standards. Mass spectra were taken on LKB-900 and Finnigan MAT 95 (CI) instruments.

3.1. *X-Ray diffraction analysis of complexes III–V*

X-Ray diffraction data for **III–V** were measured using automated diffractometers (20°C, λ Mo$K\alpha$, $\theta/2\theta$-scans, graphite monochromator), the H atoms being located objectively and their contributions towards F_{calc} with fixed positional and thermal parameters taken into account. The crystal data and some parameters of the X-ray studies are listed in Table 7. Atomic coordinates for the structures of complexes **III–V** are listed in Tables 8–10.

TABLE 9. Atomic coordinates in complex **IV**

Atom	x	y	z
Ti	0.43834(7)	0.57334(5)	0.24961(3)
Si(1)	0.2150(1)	0.9038(1)	0.13016(5)
Si(2)	0.1522(1)	0.8678(1)	0.36835(5)
C(1)	0.2943(4)	0.7690(3)	0.2096(2)
C(2)	0.2722(4)	0.7587(3)	0.2880(2)
C(3)	0.2577(5)	0.8333(4)	0.0320(2)
C(4)	0.2971(5)	1.0600(4)	0.1131(2)
C(5)	−0.0066(5)	0.9729(4)	0.1575(2)
C(6)	0.2186(5)	0.7993(4)	0.4661(2)
C(7)	0.1663(5)	1.0529(4)	0.3427(2)
C(8)	−0.0651(5)	0.8750(5)	0.3855(2)
C(9)	0.7160(4)	0.4683(3)	0.2644(2)
C(10)	0.7157(4)	0.5240(3)	0.1832(2)
C(11)	0.6582(4)	0.6707(3)	0.1799(2)
C(12)	0.6226(4)	0.7056(3)	0.2594(2)
C(13)	0.6520(4)	0.5800(3)	0.3116(2)
C(14)	0.8063(5)	0.3248(3)	0.2944(2)
C(15)	0.7972(5)	0.4503(4)	0.1094(2)
C(16)	0.6667(5)	0.7708(4)	0.1039(2)
C(17)	0.5778(5)	0.8501(3)	0.2818(2)
C(18)	0.6411(5)	0.5679(4)	0.4008(2)
C(19)	0.2040(4)	0.5020(3)	0.2417(2)
C(20)	0.3349(4)	0.4292(3)	0.1884(2)
C(21)	0.4427(4)	0.3358(3)	0.2338(2)
C(22)	0.3807(4)	0.3561(3)	0.3157(2)
C(23)	0.2340(4)	0.4585(3)	0.3202(2)
C(24)	0.0546(5)	0.5975(4)	0.2191(2)
C(25)	0.3505(5)	0.4380(4)	0.0994(2)
C(26)	0.5746(5)	0.2175(4)	0.2015(2)
C(27)	0.4397(5)	0.2669(4)	0.3877(2)
C(28)	0.1186(5)	0.4926(4)	0.3973(2)

TABLE 10. Atomic coordinates in complex **V**

Atom	x	y	z
Ti	0.1998(1)	0.2295(1)	0.2701(1)
Si	0.4912(1)	−0.1157(1)	0.2829(1)
C(1)	0.3993(2)	0.0612(2)	0.2545(1)
C(2)	0.4291(2)	0.1595(2)	0.2001(1)
C(3)	0.5607(2)	0.1882(2)	0.1339(1)
C(4)	0.7088(2)	0.1192(2)	0.1344(2)
C(5)	0.8322(2)	0.1505(3)	0.0727(2)
C(6)	0.8107(3)	0.2477(3)	0.0095(2)
C(7)	0.6649(3)	0.3179(3)	0.0073(2)
C(8)	0.5432(2)	0.2888(2)	0.0693(2)
C(9)	0.2845(2)	0.2700(2)	0.3939(1)
C(9a)	0.4159(3)	0.1774(2)	0.4231(2)
C(10)	0.2937(2)	0.3778(2)	0.3327(2)
C(10a)	0.4334(3)	0.4230(2)	0.2906(2)
C(11)	0.1437(2)	0.4512(2)	0.3310(2)
C(11a)	0.1042(3)	0.5834(2)	0.2822(2)
C(12)	0.0423(2)	0.3886(2)	0.3929(1)
C(12a)	−0.1260(2)	0.4503(2)	0.4314(2)
C(13)	0.1302(2)	0.2740(2)	0.4288(1)
C(13a)	0.0710(3)	0.1797(3)	0.4992(2)
C(14)	−0.0217(2)	0.3106(2)	0.2118(1)
C(14a)	−0.1478(2)	0.4414(2)	0.2203(2)
C(15)	−0.0284(2)	0.1892(2)	0.2616(1)
C(15a)	−0.1561(2)	0.1679(2)	0.3380(2)
C(16)	0.0955(2)	0.0826(2)	0.2139(1)
C(16a)	0.1143(2)	−0.0652(2)	0.2348(2)
C(17)	0.1765(2)	0.1375(2)	0.1364(1)
C(17a)	0.3073(2)	0.0578(2)	0.0638(2)
C(18)	0.1081(2)	0.2787(2)	0.1362(1)
C(18a)	0.1448(3)	0.3760(2)	0.0620(2)
C(19)	0.6741(3)	−0.1423(2)	0.3123(2)
C(20)	0.5418(3)	−0.2306(2)	0.1861(2)
C(21)	0.3654(3)	−0.1786(2)	0.3832(2)

3.2. *Synthesis of complex II*

Cp_2TiCl_2 (1 g, 4.0 mmol), 0.1 g (4.1 mmol) of finely shaved magnesium and 0.92 ml (4.1 mmol) of bis(trimethylsilyl)acetylene in 25 ml of THF were stirred at room temperature under Ar for 3 h, after which the resulting dark solution was filtered and evaporated *in vacuo* to dryness at room temperature. The residue was dissolved in 20 ml of hexane and the solution again filtered. Cooling the hexane filtrate to −78°C resulted in golden-yellow crystals of complex **II** which were separated from the mother liquor by decanting and dried *in vacuo* at room temperature. The yield of **II** was 0.71 g (51%); m.p. 81–82°C (dec.) under Ar. The complex obtained was readily sublimed *in vacuo* ($\sim 10^{-4}$ Torr) at 50–60°C. Analysis: Found: C, 61.82; H, 7.98%; mol.wt. 340 (cryoscopically in C_6H_6). $C_{18}H_{28}TiSi_2$ requires: C, 62.04; H, 8.10%; mol.wt. 348. ^1H NMR (C_6D_6) δ: −0.29 (s, 18H, $SiMe_3$); 6.45 (s, 10H, η^5-C_5H_5) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6) δ: 0.59 (s, $SiMe_3$); 117.78 (s, η^5-C_5H_5); 244.70 (s, C≡C) ppm. IR

(Apiezon grease M mull) ν (cm^{-1}): 1687 (C≡C). Mass spectrum (*m/e*, 12 eV): 348 $(M)^+$; 333 $(M - Me)^+$; 178 $(Cp_2Ti)^+$; 170 $(Me_3SiC_2SiMe_3)^+$; 155 $(Me_3SiC_2SiMe_3 - Me)^+$.

3.3. Synthesis of complex III

Cp_2TiCl_2 (1 g, 4.0 mmol), 0.1 g (4.1 mmol) of finely shaved magnesium and 0.88 ml (4.4 mmol) of phenyl(trimethylsilyl)acetylene in 30 ml of THF were stirred at room temperature under Ar for 2.5 h, and the resulting dark solution (after filtration) was evaporated to dryness *in vacuo* at room temperature. The residue was dissolved in 60 ml of hexane, the yellow-brown solution filtered and the filtrate evaporated *in vacuo* until crystallization started. Subsequent cooling of the evaporated filtrate to −75°C gave brown crystals of complex **III** which were separated from the mother liquor by decanting and dried *in vacuo* at room temperature. The yield of **III** was 1 g (71%); m.p. 98–99°C (dec.) under Ar. Analysis: Found: C, 71.38; H, 6.92; Ti, 13.38%. $C_{21}H_{24}TiSi$ requires: C, 71.57; H, 6.86; Ti, 13.59%. ^1H NMR (C_6D_6) δ: −0.15 (s, 9H, $SiMe_3$); 6.31 (s, 10H, η^5-C_5H_5); 6.18–7.04 (m, 5H, Ph) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6) δ: 0.65 (s, $SiMe_3$); 116.58 (s, η^5-C_5H_5); 126.14 (s, *p*-Ph); 142.38 (s, *i*-Ph); 212.96 (s, ≡*C*–$SiMe_3$); 219.63 (s, ≡*C*–Ph). The signals of the *o*-Ph and *m*-Ph carbon atoms were shielded by that of C_6D_6. IR (Nujol mull) ν (cm^{-1}): 1686 (C≡C). Mass spectrum (*m/e*, 70 eV): 352 $(M)^+$; 337 $(M - Me)^+$; 279 $(M - SiMe_3)^+$; 178 $(Cp_2Ti)^+$; 174 $(PhC_2SiMe_3)^+$; 159 $(PhC_2SiMe_3 - Me)^+$.

3.4. Synthesis of complex IV

$Cp^*_2TiCl_2$ (3.2 g, 8.2 mmol), 0.21 g (8.6 mmol) of finely shaved magnesium and 1.83 ml (8.3 mmol) of bis(trimethylsilyl)acetylene in 40 ml of THF were stirred at room temperature under Ar for 4.5 h. The colour of the mixture changed during the course of the reaction from dark red to blue and then to dark yellow. On completion of the reaction, the solution was evaporated to dryness *in vacuo*, and the residue dissolved in 50 ml of hexane and filtered. Slow concentration of the hexane filtrate to 5–7 ml *in vacuo* resulted in yellow-brown crystals of complex **IV** which were separated by decanting, washed with 5 ml of cooled hexane and dried *in vacuo*. The yield of **IV** was 2.95 g (73%); m.p. 191–192°C (dec.) under Ar. Analysis: Found: C, 68.27; H, 9.76; Ti, 9.81%. $C_{28}H_{48}TiSi_2$ requires: C, 68.81; H, 9.90; Ti, 9.80%. ^1H NMR (C_6D_6) δ: 0.02 (s, 18H, $SiMe_3$); 1.72 (s, 30H, η^5-C_5Me_5) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6) δ: 4.18 (s, $SiMe_3$); 12.67 (s, η^5-C_5*Me*$_5$); 121.90 (s, η^5-*C*$_5Me_5$); 248.48 (s, C≡C) ppm. IR (Nujol mull) ν (cm^{-1}): 1563, 1598 (C≡C). Mass spectrum (*m/e*, 70 eV): 489 $(M)^+$; 354 $(M - Cp^*)^+$; 318 $(Cp^*_2Ti)^+$; 170 $(Me_3SiC_2SiMe_3)^+$; 155 $(Me_3SiC_2SiMe_3 - Me)^+$.

3.5. Synthesis of complex V

$Cp^*_2TiCl_2$ (3.89 g, 10 mmol), 0.25 g (10 mmol) of finely shaved magnesium and 1.74 ml (10 mmol) of phenyl(trimethylsilyl)acetylene in 50 ml of THF were stirred at room temperature under Ar for 4 h. The resulting solution was evaporated to dryness *in vacuo*, the residue dissolved in 50 ml of warm pentane and the pentane solution filtered through a G4 filter. Cooling the filtrate produced dark red crystals of complex **V** which were separated from the mother liquor, washed twice with cooled pentane and dried *in vacuo*. The yield of **V** was 3.70 g (75%); m.p. 135°C (dec.) under Ar. Analysis: Found: C, 75.38; H, 8.80; Si, 5.81; Ti, 9.87%. $C_{31}H_{44}TiSi$ requires: C, 75.58; H, 9.00; Si, 5.70; Ti, 9.72%. ^1H NMR (THF-d_8) δ: 0.00 (s, 9H, $SiMe_3$); 1.75 (s, 30H, η^5-C_5Me_5); 6.12–6.91 (m, 5H, Ph) ppm. $^{13}C\{^1H\}$ NMR (THF-d_8) δ: 3.5 (s, $SiMe_3$); 12.5 (s, η^5-C_5*Me*$_5$); 122.4 (s, η^5-*C*$_5Me_5$); 126.1 (s, *p*-Ph); 127.9 (s, *m*-Ph); 131.4 (s, *o*-Ph); 139.5 (s, *i*-Ph); 213.2 (s, ≡*C*–$SiMe_3$); 224.9 (s, ≡*C*–Ph) ppm. IR (KBr) ν (cm^{-1}): 1625 (C≡C). Mass spectrum (CI, NH_3): 493 $(M + H)^+$.

3.6. Reaction of complex II with tolane

Complex **II** (0.029 g, 0.083 mmol) was dissolved in 0.2 ml of C_6D_6 under Ar. Separately, a solution consisting of 0.015 g (0.084 mmol) of tolane in 0.6 ml of C_6D_6 was prepared. Both solutions were mixed and the resulting mixture was rapidly placed into an NMR ampoule under Ar. One or two drops of cyclohexane as an internal standard were then added to the solution and the ^1H NMR spectra of the reaction mixture recorded at known time intervals. The extent of the reaction was followed by changes in the chemical shifts and intensities of the NMR signals. Reactions of **II** with tolane at a 1:2 molar ratio or with 3-hexyne, acetone and benzophenone were carried out in a similar manner.

Acknowledgements

The authors wish to thank Dr. P.V. Petrovskii for recording and discussing the NMR spectra data and Prof. B.V. Lokshin, Dr. L. Vinogradova and Dr. S.S. Bukalov for the measurement of and help in interpreting the IR spectra.

References

1 M.E. Vol'pin, V.A. Dubovitsky, O.V. Nogina and D.N. Kursanov, *Dokl. Akad. Nauk SSSR, 151* (1963) 1100.

2 K. Sonogashira and N. Hagihara, *Bull. Chem. Soc. Jpn., 39* (1966) 1178.

3 G. Fachinetti and C. Floriani, *J. Chem. Soc., Chem. Commun.*, (1974) 66; G. Fachinetti, C. Floriani, F. Marchetti and M. Mellini, *J. Chem. Soc., Dalton Trans.*, (1978) 1398.

4 B. Demerseman and P.H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, (1981) 665.

5 B.H. Edwards, R.D. Rogers, D.J. Sikora, J.L. Atwood and M.D. Rausch, *J. Am. Chem. Soc., 105* (1983) 416.

6 H.G. Alt, H.E. Engelhardt, M.D. Rausch and L.B. Kool, *J. Am. Chem. Soc., 107* (1985) 3717.

7 V.B. Shur, S.Z. Bernadyuk, V.V. Burlakov and M.E. Vol'pin, *IInd All-Union Conf. Organomet. Chem., Abs.*, Gorky, 1982, p. 178.

8 V.B. Shur, V.V. Burlakov and M.E. Vol'pin, *J. Organomet. Chem., 347* (1988) 77.

9 S.A. Cohen and J.E. Bercaw, *Organometallics, 4* (1985) 1006.

10 B. Demerseman, R. Mahé and P.H. Dixneuf, *J. Chem. Soc., Chem. Commun.*, (1984) 1394.

11 V.V. Burlakov, U. Rosenthal, P.V. Petrovskii, V.B. Shur and M.E. Vol'pin, *Metalloorg. Khim., 1* (1988) 953; *Organomet. Chem. USSR, 1* (1988) 526.

12 V.V. Burlakov, U. Rosenthal, R. Beckhaus, A.V. Polyakov, Yu.T. Struchkov, G. Oehme, V.B. Shur and M.E. Vol'pin, *Metalloorg. Khim., 3* (1990) 476; *Organomet. Chem. USSR, 3* (1990) 237.

13 U. Rosenthal, H. Görls, V.V. Burlakov, V.B. Shur and M.E. Vol'pin, *J. Organomet. Chem., 426* (1992) C53.

14 J.L. Templeton and B.C. Ward, *J. Am. Chem. Soc., 102* (1980) 3288.

15 J.L. Templeton, *Adv. Organomet. Chem., 29* (1989) 1.

16 U. Rosenthal, G. Oehme, V.V. Burlakov, P.V. Petrovskii, V.B. Shur and M.E. Vol'pin, *J. Organomet. Chem., 391* (1990) 119.

17 F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2* (1987) S1.

18 V.B. Shur, V.V. Burlakov, A.I. Yanovsky, P.V. Petrovsky, Yu.T. Struchkov and M.E. Vol'pin, *J. Organomet. Chem., 297* (1985) 51.

19 V.B. Shur, S.Z. Bernadyuk, V.V. Burlakov, V.G. Andrianov, A.I. Yanovsky, Yu.T. Struchkov and M.E. Vol'pin, *J. Organomet. Chem., 243* (1983) 157.

20 V.B. Shur, V.V. Burlakov and M.E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1983) 1929.

21 V.B. Shur, V.V. Burlakov, A.I. Yanovsky, Yu.T. Struchkov and M.E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1983) 1212.

22 V.V. Burlakov, U. Rosenthal, A.I. Yanovsky, Yu.T. Struchkov, O.G. Ellert, V.B. Shur and M.E. Vol'pin, *Metalloorg. Khim., 2* (1989) 1193; *Organomet. Chem. USSR, 2* (1989) 633.

23 V.V. Burlakov, U. Rosenthal, F.M. Dolgushin, A.I. Yanovsky, Yu.T. Struchkov, O.G. Ellert, V.B. Shur and M.E. Vol'pin, *Metalloorg. Khim., 5* (1992) 1213, *Organomet. Chem. USSR, 5* (1992).