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Preliminary communication

CHEMISTRY OF ORGANOSILICON COMPOUNDS

CIV. SYNTHESES OF NOVEL ORGANOELEMENT HETEROCYCLES CONTAINING TITANIUM AND SILICON

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Summary

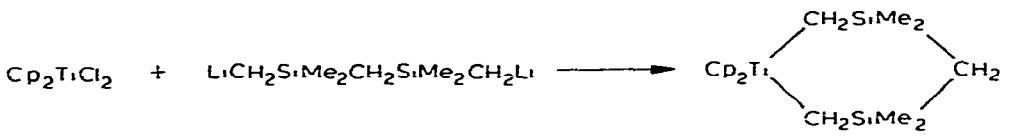
Four new dicyclopentadienyltitanium(IV) metallocycles, $Cp_2\overline{TiCH_2XCH_2}$ (X = $SiMe_2OSiMe_2$, $SiMe_2CH_2SiMe_2$, $SiMe_2SiMe_2$, and $SiMe_2SiMe_2SiMe_2$) are prepared and characterized.

There has been much interest in alkyls of the transition metals [1, 2] in recent years. However, relatively little is known about organometallic heterocycles of the transition metals which are of interest in connection with transition-metal-catalyzed cycloaddition of olefins [3]. The titanium derivatives, 1,4-tetramethylene- and 1,5-pentamethylene-dicyclopentadienyltitanium(IV) have been prepared at low temperature [4], but these compounds were characterized only through their reactions because of their thermal lability. We report the synthesis of four new organotitanium heterocycles. These compounds are thermally stable and fully characterized by spectroscopic studies.

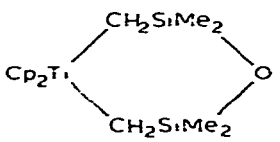
Reaction of the dilithio compound prepared from 1,5-dibromo-2,2,4,4-tetramethyl-2,4-disilapentane with a suspension of dichlorodicyclopentadienyltitanium(IV) in diethyl ether at room temperature yielded an orange-brown mixture. After evaporation of ether from the mixture, methanol was added to the residue and the resulting solution was filtered. Evaporation of methanol, extraction with ether, and then evaporation of the ether extracts gave crude, crystalline product. This was recrystallized from hexane to give the analytically pure titanium heterocyclic compound in 33% yield. All operations were carried out under argon, but the pure material was fairly stable in the air.

Three other heterocyclic compounds (II, III, and IV) were prepared in similar manner in yields of 13, 30, and 21%, respectively.

All the compounds are air stable in the pure crystalline state. Table 1 lists some physical properties and analytical data.



(I)



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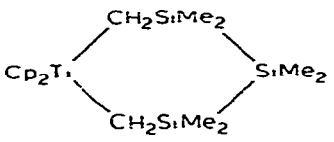

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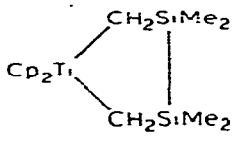


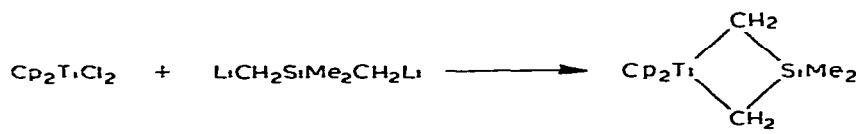
(IV)

TABLE 1

SOME PHSYICAL PROPERTIES AND ANALYTICAL DATA OF FOUR NEW ORGANOTITANIUM HETEROCYCLES

Compound	Color	M.p. (°C)	Analysis (Found (calcd.) (%))	
			C	H
I	reddish orange	88	60.78 (60.68)	8.35 (8.39)
II	yellowish orange	143—145	56.50 (56.78)	7.82 (7.74)
III	reddish orange	83—85	56.52 (56.80)	8.58 (8.47)
IV	reddish orange	134—136	59.58 (59.60)	8.28 (8.13)

We also have attempted to prepare the four-membered cyclic compound V. The reaction of Cp_2TiCl_2 with the corresponding compound gave a reddish yellow solid melting at 98—102°C. NMR spectra indicated this solid to be V, but an analytically pure sample could not be obtained due to its lability.



(V)

Mass spectra of these new heterocycles have been examined. Very weak molecular ions and a strong Cp_2Ti^+ ion were observed for all compounds. Values of *m/e* and relative intensities in % were: I: 336 (M^+, 1.9) 321 ($M^+ - CH_3$, 1.7) 178 (Cp_2Ti^+, 100) 113 ($CpTi^+$, 7.1) 73 (5.4) 28 (17.8); II: 338 (M^+, 4.6) 323 ($M^+ - CH_3$, 1.7) 310 (4.5) 178 (100) 113 (8.4) 73 (Me_3Si^+, 7.3) 28 ($CH_2{=}CH_2^+$, 10.5);

III: 380 (M^+, 1.1) 365 ($M^+ - CH_3$, 0.5) 178 (100) 113 (6.5) 73 (2.7); IV: 322 (M^+, 2.3) 307 ($M^+ - CH_3$, 0.6) 178 (100) 113 (45.8) 73 (3.3) 28 (12.4).

NMR data are listed in Table 2. Considerable solvent shifts were observed for these compounds but no change was indicated in the NMR spectrum of I at temperatures as low as $-110°$ in CS_2. Photochemical and thermal reactions of these new compounds are under study.

TABLE 2

NMR SPECTRA OF ORGANOTITANIUM COMPOUNDS

Compound	δ (ppm) in $CDCl_3$ (in C_6D_6) [c]			
	Ti—CH_2—Si	$TiCH_2$—$SiCH_3$	Cp	Other
I	0.88 (0.92)	−0.08 (0.23)	6.08 (5.82)	−0.54 (−0.32) [b]
II	0.65 (0.66)	−0.02 (0.22)	6.17 (5.89)	
III	0.43 (0.44)	−0.08 (0.22)	6.07 (5.80)	−0.11 (0.17) [c]
IV	1.23 (1.32)	−0.02 (0.30)	6.08 (5.84)	
V [d]	2.40 (2.53)	0.02 (0.09)	5.87 (5.65)	
$Cp_2Ti(CH_2SiMe_3)_2$ [e]	0.89 (0.96)	−0.06 (0.10)	6.11 (5.90)	

[a] A Varian A-60 was used. [b] Si—CH_2—Si. [c] Si—$SiCH_3$—Si. [d] The spectrum of a crude sample was taken with a Varian T-60 spectrometer, see text. [e] This sample was prepared according to the literature [5].

Acknowledgment

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