CYCLOPENTADIENYL AND RELATED ORGANO EARLY TRANSITION METAL COMPLEXES: NOVEL CHEMICAL AND STRUCTURAL ASPECTS

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ABSTRACT.—We report the chemical behaviour of pentamethylcyclopentadienyl titanium alkyls and oxo-alkyls. Cp^*TiMe_3 reacts with carboxylic acids to give titanium (IV) tricarboxylates or dimeric titanium (III) dicarboxylates depending on the molar ratio of the acid. Insertion reactions of CO, CNR and Ph_2CN_2 into Ti-Me bonds of $\text{Cp}^*\text{TiCl}_2\text{Me}$, $[\text{Cp}^*\text{TiMe Y}]_2(\mu\text{-O})$ ($\text{Y}=\text{Me}, \text{Cl}$) and $[\text{Cp}^*\text{TiMe}]_3(\mu\text{-O})_3$ are studied. The thermal decomposition of this last oxo methyl titanium trimer leads to the formation of the first reported methylidyne titanium derivative $[\text{Cp}^*\text{Ti}]_3(\mu_2\text{-O})_3(\mu_3\text{-CH})$.

Also the isolation of new alkyl titanium and zirconium metallocenes, $(\text{Me}_2\text{SiCp}_2)_2\text{M R}_2$, containing dimethylsilylene bridged-cyclopentadienyl groups is reported along with the reduction of the halotitanium derivatives and the reactions of the dimeric halotitanium (III) complexes $[(\text{Me}_2\text{SiCp}_2)_2\text{Ti}(\mu\text{-Cl})]_2$ and similar cyclopentadienyl fulvalene zirconium derivatives $[\text{CpZr}(\mu\text{-Cl})]_2(\mu\text{-C}_{10}\text{H}_8)$ with lithium phenylacetylide.

Introduction

We have reported previously a number of titanium pentamethyl cyclopentadienyl trialkyls^{1,2,3} and different types of oxoalkyls obtained during their hydrolysis^{4,5}. We have also been interested in studying new types of metallocenes containing stereorigid cyclopentadienyl rings. Here we describe novel aspects of the chemical and structural behaviour of both types of compounds.

Results and discussion

MONOCYCLOPENTADIENYL DERIVATIVES

The cyclopentadienyl titanium trialkyls are electron deficient, namely twelve-electron systems that frequently present peculiar bonding situations as shown by structural X-ray diffraction studies. They are highly reactive compounds but their reactions are frequently unselective and lead to unresolvable mixtures of compounds. The final products can be recovered when all the three Ti-C bonds are transformed as in Equations (1) with carboxylic acids. In this case the intermediate methyl carboxylates decompose under UV radiation to give dimeric titanium (III) carboxylates.

Equation 1

Compounds 1-3 were characterized by IR and NMR, 4-6 by IR and EPR spectroscopy and 1 and 6 were studied by X-ray diffraction methods, as shown in Figures 1 and 2.

Alternatively clean insertion reactions take place when the starting compounds contain only one titanium-carbon bond, such as those shown in Equations (2).

Equation 2

Complexes 7-9 were characterized by IR and NMR spectroscopy.

The high reactivity of the trialkyls can be moderated by the presence of π -donor oxo groups in the coordination sphere and this prompted us to study the hydrolysis of the halo and alkyl derivatives in order to synthesize different types of μ -oxo compounds which have been previously reported^{4,5}.

Figure 1. — View of the structure of **1** with the atomic numbering scheme. Selected bond distances (Å) and angles (°): Ti-O(1) 2.206(6), Ti-O(2) 2.133(6), Ti-O(3) 2.158(6), Ti-O(4) 2.095(7), Ti-O(5) 2.185(7), Ti-O(6) 2.135(7), O(1)-Ti-O(2) 59.06(2), O(3)-Ti-O(4) 61.4(2), O(5)-Ti-O(6) 60.0(2).

Figure 2. — View of the structure of **6** with the atomic numbering scheme. Selected bond distances (Å) and angles (°): Ti(1)-Ti(1a) 3.64(8), Ti1-O(1) 2.06(3), Ti1-O(2) 2.06(3), Ti1-O(3) 2.03(4), Ti1-O(4) 2.08(3), O(1)-C(6)-O(2) 119(1), O(3)-C(7)-O(4) 125(1).

As expected, these oxo-alkyl complexes are less reactive than the trialkyls and, therefore, much more convenient as substrates to study the different aspects of the chemical behaviour described below.

Insertion reactions

The first aim was concerned with the insertion of CO in μ -oxo methyl dimers which therefore contained a O/Ti ratio of 1/2 as shown in Equation (3).

Equation 3

No further insertion of CO was observed for **10**, even after an extended treatment with excess CO. Complexes **10-11** were characterized by NMR spectroscopy⁶. As the main products they gave isopropanol by hydrolysis, acetone by treatment with O₂ and propene by thermal decomposition.

No reaction with CO was observed when the starting compound was the μ -oxo trimer [Cp*TiMe(μ -O)]₃ according to the expected lower reactivity for a higher O/Ti ratio of 1/1.

However, when the inserted species was Ph₂CN₂, the reaction took place in two steps and a second molecule was inserted as shown in Equation (4).

Equation 4

Complexes **12-13** were characterized by NMR spectroscopy and the crystal structure for **12** was studied by X-ray diffraction methods⁷. These results confirm that Ph₂CN₂ inserts more easily than CO and in fact is able also to react with the μ -oxo trimer (eq. 5), although only one of the titanium centers reacts even after an extended treatment with excess of the ligand.

Equation 5

Thermal decomposition

An agostic Ti—C interaction, as observed in some of the reported titanium alkyls¹, is an intermediate step in an α -elimination process which would lead to the formation of an alkylidene derivative. We have studied the thermal decomposition of several of these alkyls but only unresolvable mixtures of decomposition products were obtained. The lower reactivity of the oxo-alkyl derivatives makes them more suitable substrates in the study of thermal behaviour. When a toluene solution of the μ -oxo methyl trimer is heated in a sealed tube at 200° C, CH₄ is evolved and a red solution is obtained from which red crystals of **15** were separated by evaporation.

Equation 6

Complex **15** was characterized by mass spectra and NMR spectroscopy. The study of its X-ray crystal structure is in progress.

Stereorigid metallocenes

Two types of Ti and Zr metallocenes containing stereorigid fulvalene and dimethylsilylene bridged cyclopentadienyl rings have been studied. The haloderivatives were synthesized by the reported⁸ and new methods shown in Equations (7).

Equation 7

$(\text{Me}_2\text{SiCp}_2)\text{MCl}_2$

$\nearrow \text{M}'\text{R}$

$(\text{Me}_2\text{SiCp}_2)\text{MR}_2$
 $\text{M} = \text{Ti}; \text{R} = \text{Me}, \mathbf{16}; \text{CH}_2\text{SiMe}_3, \mathbf{17};$
 $\text{CH}_2\text{Ph}, \mathbf{18}$
 $\text{R}_2 = \text{O}-(\text{CH}_2)_2\text{C}_6\text{H}_4, \mathbf{19}$
 $\text{M} = \text{Zr}; \text{R} = \text{CH}_2\text{SiMe}_3, \mathbf{20}$

$\searrow \text{M}'\text{R}$

$(\text{Me}_2\text{SiCp}_2)\text{TiRCl}$
 $\text{R} = \text{Me}, \mathbf{21}; \text{CH}_2\text{SiMe}_3, \mathbf{22};$
 $\text{SiMe}_3, \mathbf{23}$

All these compounds were characterized by visible-UV and NMR spectroscopy and crystal structures for **17** and **21** were studied by X-ray diffraction methods.

Atom	U ¹¹	U ²²	U ³³	U ¹²	U ¹³	U ²³
Si	0.0100	0.0100	0.0100	0.0000	0.0000	0.0000
Ti	0.0100	0.0100	0.0100	0.0000	0.0000	0.0000
C1	0.0100	0.0100	0.0100	0.0000	0.0000	0.0000
C2	0.0100	0.0100	0.0100	0.0000	0.0000	0.0000
C3	0.0100	0.0100	0.0100	0.0000	0.0000	0.0000
C4	0.0100	0.0100	0.0100	0.0000	0.0000	0.0000
C5	0.0100	0.0100	0.0100	0.0000	0.0000	0.0000
C6	0.0100	0.0100	0.0100	0.0000	0.0000	0.0000
C7	0.0100	0.0100	0.0100	0.0000	0.0000	0.0000
C8	0.0100	0.0100	0.0100	0.0000	0.0000	0.0000
C1a	0.0100	0.0100	0.0100	0.0000	0.0000	0.0000
C2a	0.0100	0.0100	0.0100	0.0000	0.0000	0.0000
C3a	0.0100	0.0100	0.0100	0.0000	0.0000	0.0000
C4a	0.0100	0.0100	0.0100	0.0000	0.0000	0.0000
C5a	0.0100	0.0100	0.0100	0.0000	0.0000	0.0000
Cl	0.0100	0.0100	0.0100	0.0000	0.0000	0.0000
Cl6	0.0100	0.0100	0.0100	0.0000	0.0000	0.0000

The reduction of the titanium dichloro-derivative with Na/Hg gives dimeric and monomeric titanium (III) complexes according to the following Equation (9).

These titanium (III) complexes are paramagnetic. They were characterized by EPR spectroscopy. The crystal structure of **25** was studied by X-ray diffraction.

The withdrawing of Si **3d** orbitals in these silylene bridged cyclopentadienyl complexes modifies the π -electron distribution of the ring shielding the internal C(1) atom and deshielding the remaining ring carbon atoms. This different electron distribution in the ring makes the Ti-C ring distances different in such a way that the Ti-C(1) distance is slightly shorter than those to the external carbon atoms and moreover it depends on the steric hindrance imposed by the other two titanium substituents.

Equation 10

Equation 10

Complexes **28-30** were characterized by NMR spectroscopy.

A complex of type **28** has been proposed as intermediate, and a similar derivative with $\text{C}\equiv\text{CSiMe}_3$ was isolated in a similar reaction⁹. In this case the reaction is sufficiently slow to isolate the product, although it reacts further to give **29**. The main difference between **28** and **30** is the higher alkylidene character of the acetylide carbon atom bonded to zirconium for which a resonance at 211.21 ppm is observed.

Experimental

SPECTROSCOPIC DATA FOR COMPLEXES DESCRIBED ABOVE

(1) IR $\nu_{\text{as}}(\text{OCO})$ 1610 cm^{-1} , $\nu_{\text{s}}(\text{OCO})$ 1380 cm^{-1} ; ^1H NMR (80MHz., C_6D_6 , 28° C) δ 2.05 (s, 15H, C_5Me_5), 6.55-7.66 (m, Ph).

(2) IR $\nu_{\text{as}}(\text{OCO})$ 1600 cm^{-1} , $\nu_{\text{s}}(\text{OCO})$ 1375 cm^{-1} ; ^1H NMR (80MHz., C_6D_6 , 28° C) δ 2.22 (s, 15H, C_5Me_5), 3.10 (s, 9H, OMe), 6.55-8.13 (m, 12 H, C_6H_4).

(3) IR $\nu_{\text{as}}(\text{OCO})$ 1540 cm^{-1} , $\nu_{\text{s}}(\text{OCO})$ 1371 cm^{-1} ; ^1H NMR (80MHz., C_6D_6 , 28° C) δ 1.99 (s, 15H, C_5Me_5), 1.83 (s, 9H, $-\text{OOCCH}_3$).

(4) IR $\nu_{\text{as}}(\text{OCO})$ 1655 cm^{-1} , $\nu_{\text{s}}(\text{OCO})$ 1358 cm^{-1} .

(5) IR $\nu_{\text{as}}(\text{OCO})$ 1560 cm^{-1} , $\nu_{\text{s}}(\text{OCO})$ 1350 cm^{-1} ; EPR (THF, room temp.) $g_{\text{av}} = 1.7744$.

(6) IR $\nu_{\text{as}}(\text{OCO})$ 1613 cm^{-1} , $\nu_{\text{s}}(\text{OCO})$ 1430 cm^{-1} ; EPR (THF, room temp.) $g_{\text{av}} = 1.858$.

(7) IR $\nu(\text{CO})$ 1580 cm^{-1} ; ^1H NMR (80MHz., C_6D_6 , 28° C) δ 1.77 (s, 15H, C_5Me_5), 2.10 (s, 3H, $-\text{OCMe}$); ^{13}C NMR (25MHz., C_6D_6 , 28° C) δ 12.90 (C_5Me_5), 27.28 ($-\text{OCMe}$), 129.17 (C_5Me_5).

(8) IR $\nu(\text{C}=\text{N})$ 1587 cm^{-1} ; ^1H NMR (270MHz., CDCl_3 , 28° C) δ 2.02 (s, 6H, $\text{C}_6\text{H}_3\text{Me}_2$), 2.16 (s, 15H, C_5Me_5), 2.53 (s, 3H, $-\text{N}=\text{CMe}$), 7.05 (s, 3H, $\text{C}_6\text{H}_3\text{Me}_2$); ^{13}C NMR (67.8 MHz., C_6D_6 , 28° C) δ 13.054 (C_5Me_5), 19.195 ($\text{C}_6\text{H}_3\text{Me}_2$), 20.447 ($-\text{N}=\text{CMe}$), 128.4 (C_5Me_5), 126.6, 130.2, 142.5 (C_6H_3).

(9) IR $\nu(\text{C}=\text{N})$ 1535 cm^{-1} ; ^1H NMR (80MHz., CDCl_3 , 28° C) δ 2.03 (s, 15H, C_5Me_5), 3.06 (s, 3H, $\text{C}-\text{N}(\text{Me})$), 7.30 (m, 10H, Ph); ^{13}C NMR (25MHz., CDCl_3 , 28° C) δ 12.76 (C_5Me_5), 44.87 ($\text{Ph}_2\text{CN}_2\text{Me}$), 128.64 (C_5Me_5), 127.73, 128.03, 128.74, 129.00, 130.04, 130.14 (Ph).

(15) EI-MS (70 eV) $m/z = 610$ (M^+ , 50%); ^1H NMR (C_6D_6 , 28° C) δ 1.96 (s, 45H, C_5Me_5), 12.59 (s, 1H, CH); ^{13}C NMR (C_6D_6 , 28° C) δ 11.8 (q, $J = 125.5$ Hz., C_5Me_5), 119.9 (s, C_5Me_5), 383.9 (d, $J = 138$ Hz., CH).

(16) ^1H NMR (270MHz., C_6D_6 , 28° C) δ 0.00 (s, 6H, SiMe_2), 0.17 (s, 6H, Ti-Me), 5.21 (t, $J = 2.4$ Hz., $4\text{H}\alpha$ C_5H_4), 7.08 (t, $J = 2.4$ Hz., $4\text{H}\beta$ C_5H_4); ^{13}C NMR (67.8MHz., C_6D_6 , 28° C) δ 5.63 (SiMe_2), 45.33 (Ti-Me), 101.3 [$\text{C}_1(\text{C}_5\text{H}_5)$], 115.3 [$\text{C}_3(\text{C}_5\text{H}_4)$], 125.4 [$\text{C}_2(\text{C}_5\text{H}_4)$].

(17) ^1H NMR (270MHz., C_6D_6 , 28° C) δ 0.07 (s, 6H, SiMe_2), 0.12 (s, 18H, SiMe_3), 1.00 (s, 4H, Ti- CH_2 -Si), 5.51 (t, $J = 2.3$ Hz., $4\text{H}\alpha$ C_5H_4), 7.19 (t, $J = 2.2$ Hz., $4\text{H}\beta$ C_5H_4); ^{13}C NMR (67.8MHz., 28° C) δ -5.71 (SiMe_2), 3.35 (SiMe_3), 65.2 (Ti- CH_2 -Si), 102.4 [$\text{C}_1(\text{C}_5\text{H}_4)$], 114.1 [$\text{C}_3(\text{C}_5\text{H}_4)$], 124.5 [$\text{C}_2(\text{C}_5\text{H}_4)$].

(18) ^1H NMR (270MHz., C_6D_6 , 28° C) δ -0.15 (s, 6H, SiMe_2), 2.09 (s, 4H, Ti- CH_2 -), 5.01 (t, $J = 2.4$ Hz., $4\text{H}\alpha$ C_5H_4), 7.04 (t, $J = 2.4$ Hz., $4\text{H}\beta$ C_5H_4), 6.89 (m), 7.19 (m) (Ph). ^{13}C NMR (67.8MHz., THF- d_8 , 28° C) δ -5.80 (SiMe_2), 73.5 (Ti- CH_2 -), 103.3 [$\text{C}_1(\text{C}_5\text{H}_4)$], 118.2 [$\text{C}_3(\text{C}_5\text{H}_4)$], 126.4 [$\text{C}_2(\text{C}_5\text{H}_4)$], 121.7, 127.7, 128.3, 154.5 [C_4 , C_3 , C_2 , C_1 Ph].

(19) ^1H NMR (80 MHz., C_6D_6 , 28° C) δ 0.12 (s, 6H, SiMe_2), 2.06 (s, 4H, Ti- CH_2 -), 5.06 (t, $J = 2.2$ Hz., $4\text{H}\alpha$ C_5H_4), 6.20 (t, $J = 2.2$ Hz., $4\text{H}\beta$ C_5H_4), 6.86 (m), 7.29 (m) (C_6H_4).

(20) ^1H NMR (80MHz., C_6D_6 , 28° C) δ 0.11 (s, 6H, SiMe_2), 0.17 (s, 18H, SiMe_3), 0.19 (s, 4H, Zr- CH_2 -), 5.71 (t, $J = 2.3$ Hz., $4\text{H}\alpha$ C_5H_4), 6.71 (t, $J = 2.3$ Hz., $4\text{H}\beta$ C_5H_4); ^{13}C NMR (17.8MHz., C_6D_6 , 28° C) δ -4.91 (SiMe_2), 3.70 (SiMe_3), 46.88 (Zr- CH_2 -), 99.70 [$\text{C}_1(\text{C}_5\text{H}_4)$], 111.63 [$\text{C}_3(\text{C}_5\text{H}_4)$], 120.34 [$\text{C}_2(\text{C}_5\text{H}_4)$].

(21) ^1H NMR (80MHz., C_6D_6 , 28° C) δ -0.06 (s, 3H, SiMe_2), 0.09 (s, 3H, SiMe_2), 0.98 (s, 3H, Ti-Me), 5.28 (m, $2\text{H}\alpha$, C_5H_4), 5.54 (m, $2\text{H}\alpha'$, C_5H_4), 6.90 (m, $2\text{H}\beta$, C_5H_4), 7.06 (m, $2\text{H}\beta'$, C_5H_4).

(22) ^1H NMR (80MHz., C_6D_6 , 28° C) δ 0.06 (s, 3H, SiMe_2), 0.10 (s, 3H, SiMe_2), 0.12 (s, 9H, SiMe_3), 2.22 (s, 2H, Ti- CH_2 -), 5.27 (m, $2\text{H}\alpha$, C_5H_4), 5.75 (m, $2\text{H}\alpha'$, C_5H_4), 7.09 (m, $2\text{H}\beta$, C_5H_4), 7.36 (m, $2\text{H}\beta'$, C_5H_4).

(23) ^1H NMR (80MHz., C_6D_6 , 28° C) δ -0.20 (s, 3H, SiMe_2), -0.05 (s, 3H, SiMe_2), 0.35 (s, 9H, Ti- SiMe_3), 5.32 (m, $2\text{H}\alpha$, C_5H_4), 5.60 (m, $2\text{H}\alpha'$, C_5H_4), 6.86 (m, $2\text{H}\beta$, C_5H_4), 7.57 (m, $2\text{H}\beta'$, C_5H_4).

(25) EPR (THF, room temp.) $g_{\text{av}} = 1.987$.

(27) EPR (THF, room temp.) $g_{\text{av}} = 1.9756$.

(28) ^1H NMR (80MHz., C_6D_6 , 28° C) δ 0.20 (s, 6H, SiMe_2), 0.37 (s, 6H, SiMe_2), 5.34 (m, 4H, C_5H_4), 5.43 (m, 4H, C_5H_4), 5.58 (m, 4H, C_5H_4), 5.70 (m, 4H, C_5H_4), 7.26 (m, Ph).

(29) ^1H NMR (80MHz., C_6D_6 , 28° C) δ 0.7 (s, 12H, SiMe_2), 5.09 (br., 4H, C_5H_4), 5.22 (br. 4H, C_5H_4), 6.15 (br., 4H, C_5H_4), 6.24 (br., 4H, C_5H_4), 7.48 (m, Ph).

(30) ^1H NMR (80MHz., C_6D_6 , 28° C) δ 4.73 (t, 4H C_{10}H_8), 5.05 (br., 4H, C_{10}H_8), 5.55 (s, 10H, C_5H_5), 7.28 (m), 7.60 (m) (Ph). ^{13}C NMR (67.8MHz., C_6D_6 , 28° C) δ 98.10 [$\text{C}_2(\text{C}_{10}\text{H}_8)$], 102.9 [$\text{C}_3(\text{C}_{10}\text{H}_8) + \text{C}_5\text{H}_5$], 106.7 [$\text{C}_1(\text{C}_{10}\text{H}_8)$], 127.14, 129.5, 131.61, 135.50 (Ph), 143.97 ($-\text{C}\equiv\text{C}-\text{Ph}$), 211.21 ($-\text{C}\equiv\text{C}-\text{Ph}$).

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