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SYNTHESIS AND REACTIVITY OF CYCLOPENTADIENYLTITANIUM COMPLEXES OF THE POLYDENTATE ALKOXIDE LIGAND *CIS*-1,3,5-CYCLOHEXANETRIALKOXIDE

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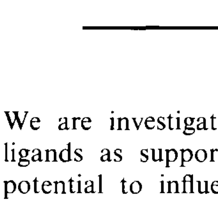
Abstract—*Cis*-1,3,5-cyclohexanetriol [$C_6H_9(OH)_3$] reacts with η^5-$(C_5R_5)TiCl_3$ [$R_5 = H_5$, Me_5, $(Me_3Si)(H)_4$, 1,3-$(Me_3Si)_2(H)_3$, (1,3-$(t\text{-}Bu)_2(H)_3$] in the presence of three molar equivalents of triethylamine, affording substituted cyclopentadienyltitanium *cis*-1,3,5-cyclohexanetrialkoxide complexes with an adamantane-type structure. The complex η^5-$(C_5Me_5)Ti(O_3C_6H_9)$ is thermally stable to 220°C in the solid state, and a benzene solution of the complex η^5-(1,3-t-$Bu_2C_5H_3)Ti(O_3C_6H_9)$ is stable to cleavage of the alkoxide ligand by three equivalents of H_2O for more than 3 h. Attempts to cleave 1,3-t-$Bu_2C_5H_4$ from η^5-(1,3-t-$Bu_2C_5H_3)Ti(O_3C_6H_9)$ with electrophiles H^+ and Br_2 are reported.

We are investigating unique chelating alkoxide ligands as supporting ligands, because of their potential to influence the reactivity of a metal centre. Group 4 and 5 transition-metal complexes of monodentate alkoxide ligands have demonstrated novel reactivity and structural features, some of which are relevant to catalysis and to metal oxides.[1,2] However, complexes of tri- and higher-dentate chelating alkoxide ligands remain relatively unexplored.[2] We previously communicated the synthesis and molecular structure of η^5-(1,3-bis(trimethylsilyl)cyclopentadienyl)titanium *cis*-1,3,5-cyclohexanetrialkoxide (**1**), in which the trialkoxide ligand is moderately stable to displacement by monodentate alcohols (e.g. MeOH, EtOH).[1a]



1, R^1=R^3=Me_3Si; R^2=R^4=R^5=H
2, $R^{1\text{-}5}$=Me
3, R^1=Me_3Si; $R^{2\text{-}5}$=H
4, $R^{1\text{-}5}$=H
5, R^1=R^3=*t*-Bu; R^2=R^4=R^5=H

We are interested in the stability of *cis*-1,3,5-cyclohexanetrialkoxide as a supporting ligand. Thus, it is of interest to replace the Cp′ ligand of $Cp'Ti(O_3C_6H_9)$ with other, more reactive ligands and determine whether the *cis*-1,3,5-cyclohexanetrialkoxide complex remains stable enough to isolate.

Herein we report the synthesis of substituted cyclopentadienyl compounds analogous to **1**, $Cp'Ti(O_3C_6H_9)$ (**2**–**5**) and attempts to cleave the cyclopentadienyl group of **1**–**5** in order to study the reactivity of titanium (IV) coordinated by *cis*-1,3,5-cyclohexanetrialkoxide.

EXPERIMENTAL

Reagents, solvents and general procedures

Unless otherwise stated, all operations were conducted under high purity nitrogen using standard Schlenk techniques. The following were obtained from commercial sources and used without further purification: n-butyllithium, cyclohexanol (Aldrich); 1,3-di-t-butylcyclopentadiene (Quantum Design). The compounds Me_3SiCl (Aldrich), pentamethylcyclopentadiene (Aldrich) and $TiCl_4$

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(Strem) were distilled prior to use, while η^5-$(C_5H_5)TiCl_3$ (Aldrich) was recrystallized from benzene and η^5-$(C_5Me_5)TiCl_3$ (Strem) was sublimed. Benzene (Fisher) was distilled from potassium or dried over 4 Å molecular sieves (Linde) and toluene (Fisher) was distilled from sodium. Hexane (American Scientific) and tetrahydrofuran (Aldrich) were distilled from sodium/potassium alloy. Methylene chloride (Fisher) was distilled from phosphorus pentoxide or dried over 4 Å molecular sieves (Linde) and Et_3N (Aldrich) was distilled from calcium hydride and stored over 4 Å molecular sieves (Linde). *Cis*-1,3,5-cyclohexanetriol[3] was recrystallized from 95% EtOH and dried at 110°C for 12 h prior to use.

Analytical procedures

Elemental analyses were performed by the University Instrumentation Center at the University of New Hampshire and by Pascher Microanalytical Laboratory (Remagen, Germany). IR spectra were measured from mineral oil (Nujol) mulls between KBr plates or from KBr pellets on a Perkin–Elmer 283B spectrometer and were referenced to the 1028 cm^{-1} band of a 0.05-mm polystyrene film. Absorptions are described below as follows: strong (s), medium (m), weak (w), shoulder (sh) and broad (br). ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-360 spectrometer (360 and 90 MHz, respectively) and were referenced internally to tetramethylsilane. Mass spectra were obtained on a Hewlett–Packard 5890 mass spectrometer.

Preparation of η^5-$(1,3\text{-t-}Bu_2C_5H_3)TiCl_3$[4]

The reaction between di-tert-butyltrimethylsilylcyclopentadiene[5] and $TiCl_4$ was similar to the literature preparation with the substitution of benzene as the reaction solvent and toluene for recrystallization. The identification was confirmed by ^1H NMR. ^1H NMR (C_6D_6, 25°C): δ 6.64 (t, $J = 2.5$ Hz, 1H, C_5H_3); 6.21 (d, $J = 2.5$ Hz, 2H, C_5H_3); 1.11 (s, 18H, —$C(CH_3)_3$).

Preparation of η^5-$[1,3\text{-}(Me_3Si)_2C_5H_3]TiCl_3$[6]

The reaction between $(Me_3Si)_3C_5H_3$[7] and $TiCl_4$ was similar to the literature preparation with the substitution of benzene as the reaction solvent and toluene for recrystallization. The identification was confirmed by ^1H NMR. ^1H NMR (C_6D_6, 25°C): δ7.25 (m, 1H, C_5H_3); 6.80 (d, $J = 2.6$ Hz, 2H, C_5H_3); 0.26 (s, 18H, —$Si(CH_3)_3$).

Preparation of η^5-$(C_5H_5)Ti(O_3C_6H_9)$ (**4**)

Dropwise addition of η^5-$(C_5H_5)TiCl_3$ (1.94 g, 8.84×10^{-3} mol) in THF (100 cm^3) over 10 min to a stirred mixture of *cis*-1,3,5-cyclohexanetriol (1.18 g, 8.93×10^{-3} mol) and triethylamine (3.75 cm^3, 0.0270 mol) in THF (125 cm^3) gave a milky yellow suspension. After stirring for 3.5 h, $Et_3N \cdot HCl$ was filtered off and the filtrate was reduced to *ca* 40 cm^3 under reduced pressure and cooled to −30°C. A 0.45-g [21%, 1.86×10^{-3} mol, m.p. 173–175°C (dec)] yield of pale yellow prisms was obtained. Found: C, 54.4; H, 6.1. Calc. for $C_{11}H_{14}O_3Ti$: C, 54.6; H, 6.4%. IR (KBr pellet, 300–4000 cm^{-1}): 332 (m), 390 (m), 435 (m), 465 (m), 590 (s, br), 630 (s), 770 (s), 810 (s, br), 875 (s), 910 (s), 1005 (s), 1050 (w, sh), 1080 (s, br), 1170 (w), 1220 (s), 1285 (s), 1330 (m), 1340 (m), 1358 (w), 1420 (s), 1435 (m), 2930 (s, br), 3090 (m) cm^{-1}. ^1H NMR (C_6D_6, 25°C): δ 6.54 (s, 5H, C_5H_5); 4.65 (m, 3H, —OCH—); 1.48 [d of m, $J = 13$ Hz, 3H, —$OCH(CH_2)$]; 1.37 [d of m, $J = 13$ Hz, 3H, —$OCH(CH_2)$]. $^{13}C\{^1H\}$ NMR (C_6D_6, 25°C): 114.84 (s, C_5H_5); 74.43 (s, —OCH—); 36.27 (s, —CH_2—). MS (EI, 70 eV): 242 (M^+).

Preparation of η^5-$(C_5Me_5)Ti(O_3C_6H_9)$ (**2**)

Dropwise addition of η^5-$(C_5Me_5)TiCl_3$ (0.800 g, 2.76×10^{-3} mol) in THF (50 cm^3) over 40 min to a stirred mixture of *cis*-1,3,5-cyclohexanetriol (0.369 g, 2.79×10^{-3} mol) and triethylamine (1.16 cm^3, 8.36×10^{-3} mol) in THF (100 cm^3) gave a milky yellow suspension. After stirring for 3 h the $Et_3N \cdot HCl$ was filtered off and solvent was removed from the filtrate under reduced pressure, leaving a pale yellow residue which was crystallized from toluene–hexane (*ca* 2:1 v/v) at −78°C. A 0.46-g (53%, 1.47×10^{-3} mol, m.p. 195–197°C) yield of pale yellow prisms was obtained. Found: C, 61.6; H, 7.4. Calc. for $C_{16}H_{24}O_3Ti$: C, 61.5; H, 7.8%. IR (KBr pellet, 300–4000 cm^{-1}): 315 (w), 415 (m), 453 (w), 583 (s, br), 625 (s), 760 (s), 802 (w), 875 (s), 913 (m), 1000 (m), 1090 (s, br), 1175 (w, br), 1215 (m), 1280 (m), 1315 (w), 1330 (w), 1378 (m), 1415 (w), 1430 (w, sh), 1485 (w), 2880 (s), 2915 (s) cm^{-1}. ^1H NMR (C_6D_6, 25°C): δ 4.59 (m, 3H, —OCH—); 2.15 [s, 15H, $C_5(CH_3)_5$]; 1.41–1.51 [m, 6H, —$OCH(CH_2)$—]. $^{13}C\{^1H\}$ NMR (C_6D_6, 25°C): δ 123.29 [s, $C_5(CH_3)_5$]; 73.11 (s, —OCH—); 37.57 [s, —$OCH(CH_2)$—]; 11.26 [s, $C_5(CH_3)_5$]. MS (EI, 70 eV): 312 amu (M^+).

Preparation of η^5-$[Me_3SiC_5H_4]Ti(O_3C_6H_9)$ (**3**)

Cis-1,3,5-cyclohexanetriol (0.23 g, 1.7×10^{-3} mol) was dissolved in THF (105 cm^3) and the solution was dried for 2 h over molecular sieves. The triol solution was transferred to a flask and Et_3N (0.72 cm^3, 5.1×10^{-3} mol) was added with stirring. To this solution, η^5-$(Me_3SiC_5H_4)TiCl_3$[8] (0.51 g, 1.7×10^{-3} mol) in THF (20 cm^3) was added dropwise. A white precipitate ($Et_3N \cdot HCl$) formed immediately. When addition was complete, stirring was continued for an additional 1.5 h. The yellow supernatant was filtered, the precipitate was washed with THF (40 cm^3), and the combined liquid was evaporated to dryness under reduced pressure affording yellow oil and solid. This material was triturated with hexane (20 cm^3). Sublimation of the residue (0.001 Torr, 90–130°C, 5.5 h) yielded pale orange microcrystals (0.059 g, 1.8×10^{-4} mol, 11%). ^1H NMR (C_6D_6, 25°C): δ 0.36 [s, 9H, $Si(CH_3)_3$]; 1.32–1.45 [m, 6H, —$OCH(CH_2)$—]; 4.61 (m, 3H, —OCH—); 6.74 (s, 4H, C_5H_4).

Preparation of η^5-$[1,3\text{-}(Me_3Si)_2C_5H_3]Ti(O_3C_6H_9)$ (**1**)

Cis-1,3,5-cyclohexanetriol (0.67 g, 5.1×10^{-3} mol) was dissolved in THF (300 cm^3) and the solution was dried over molecular sieves for 2 h. The solution was transferred to a flask and Et_3N (2.1 cm^3, 0.015 mol) was added with stirring. To this solution, η^5-$[1,3\text{-}(Me_3Si)_2C_5H_3]TiCl_3$ (1.85 g, 5.07×10^{-3} mol) in THF (80 cm^3) was added dropwise over 1 h. A fine white precipitate ($Et_3N \cdot HCl$) formed immediately. When the addition was complete, the mixture was stirred for an additional 1 h at room temperature. The reaction mixture was filtered and the precipitate was washed with THF (45 cm^3). The washing was combined with the filtrate and the solvent was removed under reduced pressure, yielding a yellow microcrystalline solid from which pale yellow needles were obtained by crystallization from hexane at −78°C. A 0.60-g (31%, 1.69×10^{-3} mol, m.p. 125–126°C) yield was obtained. Found: C, 52.8; H, 7.9. Calc. for $C_{17}H_{30}O_3Si_2Ti$: C, 52.8; H, 7.8%. IR (Nujol, 400–4000 cm^{-1}): 410 (m), 438 (s), 458 (w), 473 (m), 596 (s), 623 (s), 631 (s), 643 (s), 693 (w), 758 (s), 768 (s), 838 (s), 883 (s), 893 (w, sh), 913 (m), 923 (s), 928 (w, sh), 1003 (m), 1010 (m), 1053 (m), 1098 (s), 1163 (w, br), 1218 (s), 1253 (s), 1290 (w), 1297 (w), 1323 (w), 1338 (w), 1400 (w), 3118 (w) cm^{-1}. ^1H NMR (C_6D_6, 25°C): δ 7.05 (t, 1H, Si—CH—Si); 6.93 (d, 2H, C_5H_3); 4.57 (m, 3H, —OCH—); 1.29–1.40 [m, 6H, —$OCH(CH_2)$]; 0.39 [s, 18H, $Si(CH_3)_3$]. $^{13}C\{^1H\}$ NMR (C_6D_6, 25°C): δ 131.19, 127.08, 124.11 (s, C_5H_3); 74.13 (s, —OCH—); 36.15 [s, —$OCH(CH_2)$—]; −0.20 [s, $Si(CH_3)_3$]. MS (EI, 70 eV): 386 amu (M^+).

Preparation of η^5-$(1,3\text{-}t\text{-}Bu_2C_5H_3)Ti(O_3C_6H_9)$ (**5**)

Dropwise addition, over 30 min, of η^5-$(1,3\text{-}t\text{-}Bu_2C_5H_3)TiCl_3$ (1.87 g, 5.61×10^{-3} mol) in THF (60 cm^3) to a stirred mixture of *cis*-1,3,5-cyclohexanetriol (0.749 g, 5.67×10^{-3} mol) and triethylamine (2.38 cm^3, 0.0171 mol) in THF (150 cm^3) gave a milky yellow suspension. After stirring for 3 h, the $Et_3N \cdot HCl$ was filtered off and solvent removed under reduced pressure, leaving a white crystalline residue which was purified by recrystallization from hexane at −30°C. A 1.25-g (62%, 3.51×10^{-3} mol, m.p. 153–154°C) yield of white needles was obtained. Found: C, 64.7; H, 7.5. Calc. for $C_{19}H_{30}O_3Ti$: C, 64.9; H, 7.8%. IR (KBr pellet, 300–4000 cm^{-1}): 330 (m), 390 (m), 435 (s), 460 (m), 585 (s, br), 630 (s), 670 (m), 690 (m), 765 (s), 835 (s), 880 (s), 915 (m), 1005 (s), 1095 (s, br), 1215 (s), 1255 (m), 1295 (m), 1330 (m), 1340 (m), 1365 (s), 1375 (s), 1425 (m), 1465 (m), 1495 (w), 2950 (s, br), 3090 (m) cm^{-1}. ^1H NMR (C_6D_6, 25°C): δ 6.52 (t, $J = 2.6$ Hz, 1H, C_5H_3); 6.41 (d, $J = 2.6$ Hz, 2H, C_5H_3); 4.65 (m, 3H, —OCH—); 1.43 [s, 18H, —$C(CH_3)_3$]; 1.35–1.49 [m, 6H, —$OCH(CH_2)$]. $^{13}C\{^1H\}$ NMR (C_6D_6, 25°C): δ 144.02 [s, —CHC(t-Bu)CH—]; 110.49 [s, —$(CH)_2$—]; 108.82 (s, —CH—); 73.98 (s, —OCH—); 36.62 [s, —$OCH(CH_2)$—]; 33.01 [s, —$C(CH_3)_3$]; 31.54 (s, —CH_3). MS (EI, 70 eV): 354 amu (M^+).

Solid-state pyrolysis of η^5-$(C_5Me_5)Ti(O_3C_6H_9)$ (**2**)

Compound **2** (0.23 g) was heated to 210°C under nitrogen (13.6 atm pressure to reduce sublimation) in a sealed bottle for 1.5 h. White needles sublimed from **2**, while a pale green melt remained. After cooling, analysis of the needles and the melt by mass and ^1H NMR spectroscopy indicated no detectible reaction.

Attempted reaction (NMR sample scale) of η^5-$(1,3\text{-}t\text{-}Bu_2C_5H_3)Ti(O_3C_6H_9)$ *with water*

Two molar equivalents of water were added to η^5-$(1,3\text{-}t\text{-}Bu_2C_5H_3)Ti(O_3C_6H_9)$ (*ca* 25 mg in C_6D_6). There was no change in the NMR spectrum over a 3-h time period.

Reaction (NMR sample scale) of η^5-$(1,3\text{-}t\text{-}Bu_2C_5H_3)Ti(O_3C_6H_9)$ *with* CF_2HCO_2H

Compound **5** (20 mg) was reacted with *ca* 1.5 molar equivalents of CF_2HCO_2H in C_6D_6. After 25 h, the following ^1H NMR spectra (25°C, C_6D_6) were obtained. New complex: δ 1.75 [d, —$OCH(CH_2)$]; 4.04 (s, —OCH—); uncomplexed $1,3\text{-}t\text{-}Bu_2C_5H_4$: δ

1.12 [s, —$C(CH_3)_3$]; 2.87 (s, C_5H_4); 5.80 (s, C_5H_4); 6.08 (s, C_5H_4); compound **5**: δ 1.38 [s, —$C(CH_3)_3$]; 4.52 (s, —OCH—); 6.41 (d, C_5H_3); 6.65 (t, C_5H_3). The spectrum contains less than 19% of other peaks, at 0.58–1.00 ppm, as referenced to the intensity of the free 1,3-t-$Bu_2C_5H_4$. The integration of the new complex signals indicates more than a 35% conversion to the new complex.

RESULTS AND DISCUSSION

Reactions of cyclopentadienyltitanium trichlorides with *cis*-1,3,5-cyclohexanetriol were carried out in THF in the presence of triethylamine. The products were obtained, in 10–65% yields, by crystallization from hexane or by sublimation.

$$Cp'TiCl_3 + (HO)_3C_6H_9 + 3Et_3N \longrightarrow Cp'Ti(O_3C_6H_9) + 3Et_3NHCl$$

$$\begin{array}{lll} Cp' = & (1,3\text{-}Me_3Si)_2C_5H_3 & \mathbf{1} \\ & C_5Me_5 & \mathbf{2} \\ & Me_3SiC_5H_4 & \mathbf{3} \\ & C_5H_5 & \mathbf{4} \\ & (1,3\text{-t-Bu})_2C_5H_3 & \mathbf{5} \end{array}$$

The products are stable for over a week in dry air. They are freely soluble in hydrocarbons and ethers. Compound **2** is stable up to 220°C under nitrogen.

Because of the possibility of triequatorial coordination of *cis*-1,3,5-cyclohexanetrialkoxide to form a polymeric structure, reactions were initially carried out using dilute solutions of triol. However, later compounds were prepared using a suspension of triol in minimal solvent volume, negating this concern.

In order to examine the influence of *cis*-1,3,5-cyclohexanetrialkoxide upon the reactivity of a titanium centre, it is necessary to create titanium coordination sites by removing the cyclopentadienyl ring from one of compounds **1**–**5**. A number of reagents, including the electrophiles H^{+}[9] and Br_2,[10] and nucleophiles such as PMe_3,[11] are reported to cleave a cyclopentadienyl group from a transition metal. As demonstrated previously[1a] and in this work, the *cis*-1,3,5-cyclohexanetrialkoxide ligand is not cleaved from titanium in **4** upon treatment with three equivalents of methanol or ethanol or four equivalents of water for 2 h, so it is reasonable to attempt cleavage of Cp′ from **5** using acid. Cleavage of 1,3-t-Bu_2CpH from **5** using one molar equivalent of difluoroacetic acid was successful, as observed by ^1H NMR spectroscopy. Attempts to scale-up this reaction and isolate the acid-reacted product were unsuccessful.

$$\mathbf{5} + CF_2HCO_2H \xrightarrow[25\,h]{C_6D_6} [(CF_2HCO_2)Ti(O_3C_6H_9)] + 1,3\text{-t-}Bu_2CpH.$$

Signals for free 1,3-t-Bu_2CpH and for a new coordinated trialkoxide ligand, presumably that of "$(CF_2HCO_2)Ti(O_3C_6H_9)$," gradually increased as those for **5** decreased in a fairly clean reaction. However, the final product could not be isolated from these benzene solutions, and no assignments could be made from the ^1H NMR spectrum of the titanium product after crystallization attempts, nor could the cleavage product be stabilized through addition of Lewis bases such as pyridine.

CONCLUSION

A number of stable titanium complexes of *cis*-1,3,5-cyclohexanetrialkoxide have been prepared. ^1H NMR spectroscopy suggests that acid reaction of η^5-$(1,3\text{-t-}Bu_2C_5H_3)Ti(O_3C_6H_9)$ proceeds cleanly, but only 1,3-t-Bu_2CpH may be isolated from the reaction. Further studies of the stability of the *cis*-1,3,5-cyclohexanetrialkoxide–metal bond, and of other complexes of this trialkoxide ligand, are in progress.

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