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FORMATION AND MOLECULAR STRUCTURE OF PERMETHYLYTTROCENE METHYL TETRAHYDROFURANATE

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Summary

The reaction of $\text{Cp}_2^*\text{YCl} \cdot \text{THF}$ with MeLi in THF at -80°C gives the monomeric $\text{Cp}_2^*\text{YMe} \cdot \text{THF}$ (**1**), which has been characterized by spectroscopy, elemental analyses and a single crystal X-ray diffraction study. Complex **1** crystallizes in the orthorhombic space group $Pnam$ with lattice parameters a 17.881(4), b 8.621(2), c 15.095(3) Å, $Z = 4$, and D_{calc} 1.274 g cm $^{-3}$. Least-squares refinement using 1056 independent observed reflections and 117 parameters gave a final R value of 0.071. The Y–C(σ) bond distance is 2.44(2) Å. IR and NMR spectra indicate an agostic interaction between the metal center and one of the C–H bonds of the methyl ligand, but this could not be confirmed by the X-ray structure determination owing to disorder.

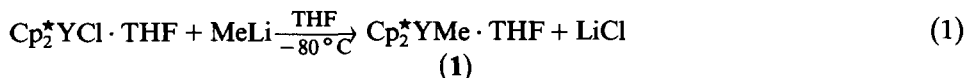
Introduction

A recent study in our laboratory of permethyltrocene derivatives [1] showed the presence of an “ α -agostic” yttrium C–H interaction [2] in the formally 14-electron complex $\text{Cp}_2^*\text{YCH}(\text{SiMe}_3)_2$. This interaction is a consequence of the electron deficiency of the metal center. An interesting question is whether such an interaction is limited to 14-electron metallocene systems or might also be observed in less electron deficient situations, such as in 16-electron complexes. We decided to synthesize a representative 16-electron complex for yttrium, viz. $\text{Cp}_2^*\text{YMe} \cdot \text{THF}$, and determine its molecular structure and the results are reported below.

Results and discussion

Synthesis and characterization

The reaction of $\text{Cp}_2^*\text{YCl} \cdot \text{THF}$ with MeLi in THF at -80°C provides a good route to salt-free $\text{Cp}_2^*\text{YMe} \cdot \text{THF}$ (**1**) (eq. 1).



Complex **1** is a colourless air-sensitive compound, and was characterized by the usual spectroscopic techniques (IR, NMR). The IR spectrum shows the expected Cp^* absorptions [1] and a weak absorption at 2770 cm^{-1} that is assigned to the $\nu(\text{C-H})$ of the methyl group on yttrium. This band indicates an α -agostic $\text{Y} \cdots \text{CH}$ interaction [2].

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows the methyl resonance at δ 21.36 ppm as a doublet ($^1J(\text{YC})$ 56.2 Hz). The small one-bond carbon hydrogen coupling ($^1J(\text{CH})$ 108.2 Hz) for this signal is substantially larger than that (84.2 Hz) observed for the static α -agostic C-H group in $\text{Cp}_2^*\text{YCH}(\text{SiMe}_3)_2$ [1]. The value of $^1J(\text{CH})$ in **1**, however, still indicates a fluxional agostic methyl group [2], since it is significantly lower than the calculated coupling constant (111.4 Hz [12]) for this interaction. The signals from the ring and methyl carbon atoms of the Cp^* ligands are at δ 115.68 and δ 11.47 ppm, respectively, normal values for permethyltrocenes.

The ^1H NMR spectrum of **1** shows the expected chemical shifts and integrations. The value of the second order yttrium coupling ($^2J(\text{YH})$ 2.3 Hz) for the methyl resonance at δ -0.66 ppm, which is the same as that observed in $\text{Cp}_2^*\text{YCH}(\text{SiMe}_3)_2$ is noteworthy.

The observation of methyl resonances as a doublet in both the ^1H and ^{13}C NMR spectra demonstrates that the complex is monomeric in solution. In the case of a dimer, coupling to the second yttrium would lead either to a triplet (symmetric bridge) [4] or a doublet of doublets (asymmetric bridge) [5] signal.

With respect to the presence of an α -agostic interaction of a methyl C-H bond with the coordinatively unsaturated yttrium atom in **1**, both IR and NMR give positive indications. The NMR data are consistent with a dynamic process in which all three C-H bonds alternate in interacting with the metal center. It was assumed that at low temperatures in the solid state this dynamic process would be frozen out and so a low temperature (100 K) X-ray study was carried out.

Crystallographic study

The orthorhombic unit cell contains four molecules which are disordered across a crystallographic mirror plane. The final positional coordinates of the non-hydrogen atoms are listed in Table 1. The molecular structure of the complex and the numbering scheme are shown in Fig. 1. Selected bond distances and bond angles are listed in Tables 2 and 3, respectively.

The two Cp^* ligands are η^5 -bonded to the yttrium atom with average distances $\text{Y}-\text{C}(\eta^5)$ 2.72(2) and 2.61(6) Å. The $\text{Y}-\text{C}(\eta^5)$ distances in **1** (2.51(3)–2.74(2) Å) are in the range of the values found in other permethyltrocenes: $\text{Cp}_2^*\text{Y}(\mu\text{-Cl})\text{YClCp}_2^*$ [6] (2.56(2)–2.69(2) Å), $\text{Cp}_2^*\text{YN}(\text{SiMe}_3)_2$ [1] (2.632(7)–2.737(7) Å), $\text{Cp}_2^*\text{YCH}(\text{SiMe}_3)_2$ [1] (2.637(6)–2.692(6) Å) and $\text{Cp}_2^*\text{Y}(\eta^2\text{-C}(3,5\text{-Me}_2\text{C}_6\text{H}_3)=\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)) \cdot \text{THF}$ [7], (2.685(3)–2.782(3) Å). The metal–ring–centroid (Cp°) distances are $\text{Cp}^\circ(1)\text{-Y}$,

TABLE 1

FINAL POSITIONAL PARAMETERS FOR THE NON-HYDROGEN ATOMS OF $\text{Cp}_2^*\text{YMe}\cdot\text{THF}$
(with esd's in parentheses)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Y	0.1132(1)	0.3673(1)	0.25(-)
O	0.2133(4)	0.5473(9)	0.2353(9)
C(1)	0.2909(6)	0.498(1)	0.232(1)
C(2)	0.3368(7)	0.638(1)	0.222(1)
C(3)	0.2865(6)	0.770(1)	0.233(1)
C(4)	0.2113(7)	0.713(1)	0.215(1)
C(5)	0.2025(7)	0.155(2)	0.265(3)
C(6)	0.0003(9)	0.401(2)	0.132(1)
C(7)	0.0254(9)	0.247(2)	0.118(1)
C(8)	0.0962(8)	0.258(1)	0.082(1)
C(9)	0.1198(9)	0.411(2)	0.071(1)
C(10)	0.059(1)	0.500(2)	0.101(1)
C(11)	-0.0808(8)	0.427(2)	0.157(1)
C(12)	-0.006(1)	0.084(2)	0.138(1)
C(13)	0.1503(9)	0.131(2)	0.047(1)
C(14)	0.187(1)	0.482(2)	0.027(1)
C(15)	0.040(1)	0.673(2)	0.103(1)
C(16)	0.0092(9)	0.328(2)	0.372(1)
C(17)	0.076(1)	0.244(2)	0.394(2)
C(18)	0.130(1)	0.358(2)	0.420(2)
C(19)	0.101(1)	0.508(2)	0.407(1)
C(20)	0.0284(9)	0.486(2)	0.376(1)
C(21)	-0.0606(8)	0.228(2)	0.364(1)
C(22)	0.0917(9)	0.076(2)	0.426(1)
C(23)	0.2080(9)	0.349(3)	0.464(1)
C(24)	0.130(1)	0.672(2)	0.426(1)
C(25)	-0.0331(9)	0.608(2)	0.363(1)

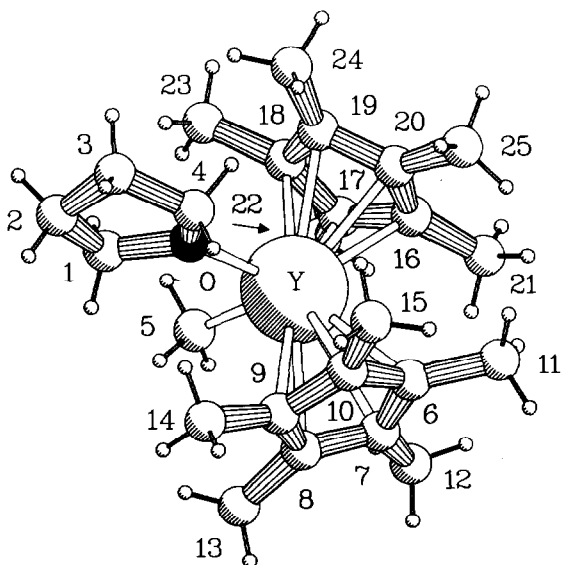


Fig. 1. The molecular structure of $\text{Cp}_2^*\text{YMe}\cdot\text{THF}$ and the adopted numbering scheme.

TABLE 2
SELECTED BOND DISTANCES (Å) FOR Cp₂*YMe·THF

Cp [*] (1) [C(6)–C(10)]		Cp [*] (2) [C(16)–C(20)]	
⟨Y–C(η ⁵)⟩	2.72(2)	⟨Y–C(η ⁵)⟩	2.61(6)
Y–Cp ^o (1)	2.444(7)	Y–Cp ^o (2)	2.32(1)
⟨C–C⟩ _{ring}	1.40(2)	⟨C–C⟩ _{ring}	1.41(2)
⟨C–CH ₃ ⟩	1.53(2)	⟨C–CH ₃ ⟩	1.54(2)
Y–C(5)	2.44(2)	C(1)–C(2)	1.47(1)
Y–O	2.379(8)	C(2)–C(3)	1.46(1)
O–C(1)	1.45(1)	C(3)–C(4)	1.46(2)
O–C(4)	1.46(1)	Y–H(51)	2.74(2)

2.444(7) and Cp^o(2)–Y, 2.32(1) Å; the angle Cp^o(1)–Y–Cp^o(2) is 137.0(3)° which is comparable with those observed in Cp₂*YCH(SiMe₃)₂, 134.4(2)° and Cp₂*YN(SiMe₃)₂, 132.2(2) and 132.4(2)°.

The THF ligand is coordinated to yttrium through the oxygen atom, the Y–O bond length is 2.379(8) Å. This is somewhat shorter than in other yttrium tetrahydrofuranates: [Cp₂*YH·THF]₂ [8], 2.460(8) Å, and Cp₃Y·THF [9], 2.451(4) Å [9]. The THF molecule forms a puckered ring, with out of plane displacements between –0.15(8) and 0.14(9) Å for the ring atoms and 0.23(6) Å for the yttrium atom.

The pseudo-tetrahedral environment of the metal center is completed by the carbon atom of the methyl ligand Y–C(5), 2.44(2) Å. This bond length is substantially shorter than those observed in the dimeric (Cp₂YMe)₂ [4], 2.553(10) and 2.537(9) Å and (Cp₂Y(η²-CH=N-t-Bu))₂ [10], 2.545(5) and 2.561(5) Å and can be compared with the Y–C distances in the monomeric complex Cp₂*YCH(SiMe₃)₂, 2.468(7) Å and the anion [Cp₂Y(CH₂SiMe₃)₂][–] [11], 2.402(6) and 2.445(6) Å.

The angle O–Y–C(5) is 90.3(4)° which is almost identical to the values observed in other metallocene THF solvates; Cp₂Lu(4-MeC₆H₄)·THF [12], 89.1(12), Cp₂YbMe·THF [13], 94.1(3) and Cp₂Lu-t-Bu·THF [14], 94.1°.

TABLE 3
SELECTED BOND ANGLES (°) FOR Cp₂*YMe·THF

O–Y–C(5)	90.3(4)
Cp ^o (1)–Y–O	102.4(4)
Cp ^o (2)–Y–O	107.6(4)
Cp ^o (1)–Y–C(5)	109(1)
Cp ^o (2)–Y–C(5)	101(1)
Cp ^o (1)–Y–Cp ^o (2)	137.0(3)
Y–C(5)–H(51)	97(2)
Y–C(5)–H(52)	108(2)
Y–C(5)–H(53)	123(1)
Y–O–C(1)	122.1(6)
Y–O–C(4)	129.7(6)
C(1)–O–C(4)	107.6(8)
O–C(1)–C(2)	107.3(8)
O–C(4)–C(3)	105.5(9)
C(1)–C(2)–C(3)	107(1)
C(2)–C(3)–C(4)	106.5(8)

The crystallographic study was undertaken in order to determine unequivocally whether there is an α -agostic methyl group in **1**. Ibers [15] has already noted the difficulties which are experienced in the exact location of hydrogen atoms in X-ray structure determinations, especially when the hydrogen atom is close to a heavy metal atom. In the complex under discussion this is even more complicated, since there is disorder in the crystalline state, and so the positions of the hydrogen atoms in **1** cannot be established accurately.

Although the smallest angle $Y-C(5)-H(51)$, $97(2)^\circ$ may not be as pronounced as the angle in $Cp_2^*YCH(SiMe_3)_2$, $84(3)^\circ$, it still is some 12° smaller than the ideal tetrahedral angle of 109° . This small angle suggests a substantial influence of the metal centre on the $C(5)-H(51)$ bond, which is tentatively interpreted as an α -agostic interaction. A neutron diffraction study on a non-disordered crystal may be required to reach a firm conclusion about this interaction.

Experimental

Manipulations were carried out under nitrogen using glovebox (Braun MB-200) and Schlenk-line techniques.

Solvents (pentane, Et_2O , THF) were dried over Na wire and distilled from Na/K alloy benzophenone ketyl prior to use. $Cp_2^*YCl \cdot THF$ [1] and MeLi [16] were prepared by published procedures. The IR spectrum (Nujol/KBr) was recorded on a Pye Unicam SP3-300 spectrophotometer and NMR spectra on a Nicolet NT-200 spectrometer. Elemental analyses were carried out at the Micro-Analytical Department of the Chemical Laboratories of the University of Groningen under supervision of Mr. A.F. Hamminga.

*Preparation of $Cp_2^*YMe \cdot THF$ (1)*

To a solution 1.35 g of $Cp_2^*YCl \cdot THF$ (2.89 mmol) in 30 ml of THF at $-80^\circ C$ was added 7.1 ml of a 0.41 M solution of MeLi in Et_2O . The mixture was stirred for 1 h then allowed to warm to room temperature. The solvents were then removed in vacuo and the white solids extracted into 50 ml of pentane. Crystallization at $-30^\circ C$ afforded 0.84 g of **1** (1.88 mmol, 65%) as colourless crystals. IR (cm^{-1}): 2770w, 2720w, 1485m, 1365m, 1340w, 1180w, 1125m, 1085m, 1050s, 1020s, 915s, 865m, 800w, 720w, 670m, 595w, 510s and 385m. 1H NMR (C_6D_6 , $25^\circ C$, TMS = δ 0.0): δ -0.66 (d, 3H, $^2J(YH)$ 2.3 Hz, YMe), 1.16 (m, 4H, β -THF), 2.00 (s, 30H, Cp^*), 3.22 (m, 4H, α -THF). $^{13}C\{^1H\}$ NMR (C_6D_6 , $25^\circ C$, TMS = δ 0.0): δ 11.47 (q, $^1J(CH)$ 124.8 Hz, C_5Me_5) 21.36 (dq, $^1J(CH)$ 108.2, $^1J(YC)$ 56.2 Hz, YMe) 24.99 (t, $^1J(CH)$ 133.1 Hz, β -THF) 69.96 (t, $^1J(CH)$ 148.7 Hz, α -THF) 115.68 (s, C_5Me_5). Anal. Found: Y, 20.17; C, 67.29; H, 9.31. $C_{25}H_{41}YO$ calc: Y, 19.91; C, 67.25; H, 9.26%.

*Data collection and structure determination of $Cp_2^*YMe \cdot THF$ (1)*

A colourless block-shaped crystal suitable for X-ray data collection was selected in a glovebox, mounted on a glass fibre, and transferred into the cold nitrogen stream of the low-temperature unit of an Enraf-Nonius CAD-4F diffractometer. Details of the data collection and structure determination are given in Table 4. Unit cell parameters were determined from a least-squares treatment of the setting angles of 16 reflections in the range $10^\circ < \theta < 12^\circ$. Data were collected for one hemi-

TABLE 4
CRYSTAL DATA AND DETAILS OF THE STRUCTURE ANALYSIS OF $\text{Cp}_2^*\text{YMe}\cdot\text{THF}$

<i>Crystal data (100 K)</i>	
Formula	$\text{C}_{25}\text{H}_{41}\text{OY}$
Mol. wt.	446.50
Crystal system	orthorhombic
Space group	<i>Pnam</i> (Nr. 62)
<i>a</i> (Å)	17.881(4)
<i>b</i> (Å)	8.621(2)
<i>c</i> (Å)	15.095(3)
<i>V</i> (Å ³)	2326.9(9)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.274
F(000)	952
μ (Mo- <i>K</i> _α) (cm ⁻¹)	25.3
Crystal size (mm)	0.13 × 0.15 × 0.30
<i>Data collection (100 K)</i>	
θ_{\min} , θ_{\max} (°)	1.14, 22.0
Radiation	Mo- <i>K</i> _α (graphite-mon.), 0.71073 Å
$\omega/2\theta$ scan (°)	0.70 + 0.35 tan θ
Horizontal and vert. aperture (mm)	4.0, 4.5
Distance crystal to detector (mm)	173
Reference reflections	$\bar{2}10$; $3\bar{2}\bar{2}$; $3\bar{2}\bar{2}$
Total data	5938
Total unique data	1488
Observed data ($I > 2.5\sigma(I)$)	1056
<i>Refinement</i>	
No. of refined parameters	117
Weighting scheme	$w = 1.0/\sigma^2(F)$
Final <i>R</i> , <i>wR</i> , <i>S</i>	0.0711, 0.0572, 2.29
$(\Delta/\sigma)_{\text{av}}$ in final cycle	0.044

sphere: $-18 \leq h \leq 18$; $-9 \leq k \leq 9$; $0 \leq l \leq 15$ and corrected for Lorentz and polarization effects and for absorption (Gaussian integration: grid $8 \times 8 \times 8$; max. and min. correction: 1.939 and 1.366). There was no indication of any decay during the 63 h of X-ray exposure time. Standard deviations based on counting statistics were increased in line with the variance of the three reference reflections: $\sigma^2(I) = \sigma_{\text{cs}}^2(I) + (0.04 I)^2$ [17]. The observed extinctions ($0kl$, $k + l = 2n + 1$; $h0l$, $h = 2n + 1$) indicate space group *Pna*2₁, or *Pnam*. The low resolution and the observed high background of the data set were taken as indications of disorder. The four sets of equivalent reflections were merged with a consistency index (on *I*) of 13.2% indicating the rather weak quality of the dataset ($\Sigma\sigma(I)/\Sigma I = 0.0778$).

The Y atom was found by direct methods (SHELXS 86, [18]), and other non-H atoms were located in subsequent difference Fourier maps. The structure was refined with a disordered model in space group *Pnam* (non-standard setting of *Pnma*) with Y occupying a special position on the *m*-mirror at $z = 1/4$ across which the other atoms are disordered. Refinement of an ordered model in *Pna*2₁ was not satisfactory; the adopted refinement of the disorder model was justified by argu-

ments similar to those in [19]. Refinement was carried out by full matrix least-squares techniques (on F) with anisotropic thermal parameters for Y and isotropic thermal parameters for the C, O atoms. Hydrogen atoms were introduced at calculated positions (C–H 0.98 Å) and included in the refinement riding on their carrier atom with one overall isotropic thermal parameter. All atoms were refined with occupational parameters of 0.50. Waser-type constraints were applied on all chemically equivalent distances. Weights were introduced in the final refinement cycles, convergence was reached at $R = 0.071$. A final difference Fourier synthesis revealed residual densities between 0.71 and $-0.61 \text{ e}/\text{Å}^3$ near Y. Neutral atom scattering factors were taken from ref. 20 and corrected for anomalous dispersion [21]. Data collection was carried out with a modified CAD-4F software package [22]. All calculations performed with SHELX76 [23] and the EUCLID package [24] (geometrical calculations and illustrations) on the CDC Cyber-855 of the University of Utrecht.

Supplementary data (all positional and thermal parameters, bond lengths, bond angles, torsion angles and a listing of structure factor amplitudes) are available from A.L.S.

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