Journal of Organometallic Chemistry, 482 (1994) 125–130

2,4-Dimethylpentadienyl complexes of neodymium, samarium and ytterbium

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(Received January 24, 1994)

Abstract

The reaction of potassium 2,4-dimethylpentadienide [K(C_7H_{11})] with $SmCl_3$ or $YbCl_3$ produced the new Complexes [$Sm^{III}(C_7H_{11})_3$] (**1**) or [$Yb^{II}(C_7H_{11})_2$(DME)] (**2**) respectively. Compound **2** could also be made with a better yield from [K(C_7H_{11})] and [$YbI_2(THF)_2$]. A fluxional process involving a η^1 form in **1** was found by variable-temperature spin saturation transfer NMR experiments. $^1J(^{171}Yb-^{13}C)$ spin–spin coupling constants have been detected for the first time, in the ^{13}C spectrum of **2** as well as in that of [$Cp_2^*Yb(THF)_2$]. Complex **2** has been characterized by X-ray crystallography which shows that the C_7H_{11} displays η^5 coordination with the Yb atom.

Key words: Ytterbium, Samarium; X-ray structure; Pentadienyl; Neodymium; Lanthanides

1. Introduction

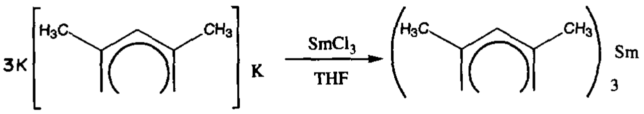
The pentadienyl ligand is now widely used in organometallic chemistry. Mostly η^5-coordinated compounds have been reported for this ligand, but η^5–η^3–η^1 transformations appear quite facile and a number of η^3 complexes have been reported [1].

On the contrary, only a few pentadienyl lanthanoid complexes have been reported with Yb [2,3], Sm [4], Nd [5,6] and Lu [7] and with η^5 or η^3 coordination of pentadienyl with the lanthanoid. Whereas tris(2,4-dimethylpentadienyl)neodymium displays tris-pentahapto coordination [5], tris(2,4-dimethylpentadienyl) lutetium has one ligand coordinated in a trihapto way and two in a pentahapto manner. This structural difference can be understood when considering that the relatively large Nd^{3+} ion is able to accommodate three η^5 ligands in its coordination sphere, whereas the relatively small Lu^{3+} cannot. η^5 and η^3 coordination has also been reported in Yb(II) chemistry [2,3].

In order to broaden the availability of the pentadienyllanthanoid complexes, we wanted first to study the interaction of Sm(III) and Yb(III) precursors with 2,4-dimethyl-pentadienyl (C_7H_{11}). We report here the syntheses of new Sm(III), Yb(II), and Nd(III) 2,4-dimethylpentadienyl complexes, and a structural study of the Yb(II) complex.

2. Results and discussion

The reaction of $SmCl_3$ with 3 equivalents of potassium 2,4-dimethylpentadienide, [K(C_7H_{11})] yields [$(C_7H_{11})_3Sm$] (**1**) as pink crystals with a 45% yield eqn. (1).



(1)

This compound is soluble in toluene or tetrahydrofuran (THF)-d_8 and the ^1H NMR spectrum in these

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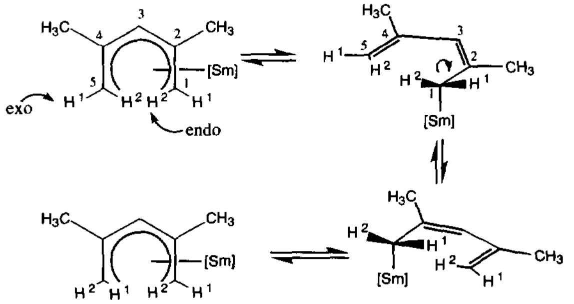
0022-328X/94/$7.00
SSDI 0022-328X(94)24647-2

solvent shows well-resolved resonances. The paramagnetic chemical shifts are temperature dependent. There is a large chemical shift difference between the signals of H(*endo*) and H(*exo*) (from 7 to 9 ppm, depending on the temperature). A singlet is obtained for the methyl resonances at 1.17 ppm at 303 K. Spin saturation transfer (SST) experiments were performed in toluene and THF. In toluene, at 363 K there is a 50% decrease in the intensity of the resonance assigned to H(*endo*) when irradiating the resonance assigned to H(*exo*), and vice versa. SST decreases smoothly with increasing temperature and is not observable at room temperature. In THF, SST is effective at room temperature and is blocked at 233 K. At 333 K in this solvent, the resonance of one H(*endo*) (or H(*exo*) had $w_{1/2} \approx 46$ Hz, the other proton resonances being obscured by the residual protons of the THF-d_8 solvent. However, no coalescence was observed.

We also prepared the known [Sm(η^8-C_8H_8)(η^5-C_7H_{11})(THF)] [4] and recorded its ^{1}H NMR spectrum. H(*endo*) and H(*exo*) resonances were well separated and we also observed SST between these protons at room temperature in THF. In toluene, however, this compound is unstable and the signal of **1** can be detected in the ^{1}H NMR spectrum.

These results point to a fluxional process that interconverts H(*endo*) and H(*exo*). A process compatible with these findings is shown in eqn. (2).



(2)

An η^3 or η ^{5}-coordinated Sm atom in **1** would be in equilibrium with a configuration in which the Sm atom is η^1 coordinated with one end of the pentadienyl

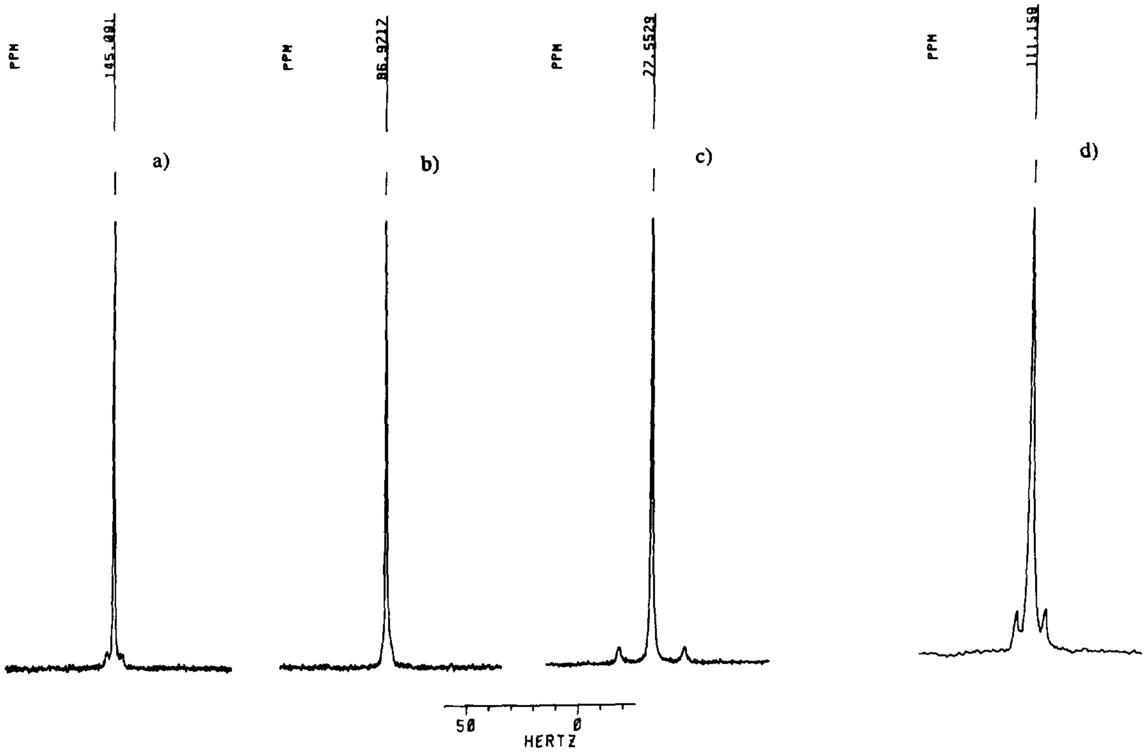
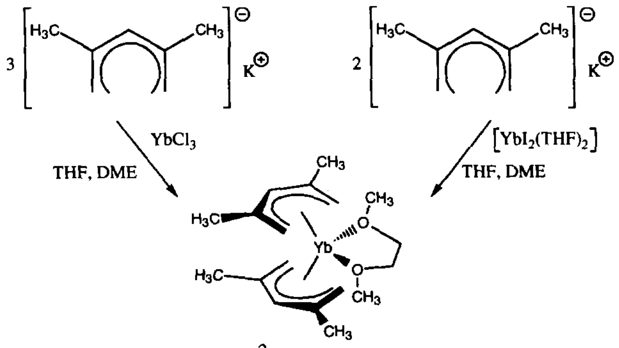


Fig. 1. ^{13}C NMR resonances at 50.32 MHz of (a) C(3), (b) C(2–4), (c) C(1–5), in [(C_7H_{11})$_2$Yb(DME)] (**2**), (d) of the η^5-Cp* ring carbon atoms in [Cp_2^*Yb(THF)$_2$]. The conditions are as follows: (a)–(c) 11000 128 K transients, no relaxation delay, 0.1 Hz line-broadening factor, digital resolution of 0.2 Hz/pt; (d) 3200 16 K transients, zero filled to 32 K, 1 s relaxation delay, 1 Hz line-broadening factor, digital resolution of 0.75 Hz/pt, sample not spinning.

system, thus inducing partial localization of the double bonds between C(2)–C(3) and C(4)–C(5) and easy rotation around the C(1)–C(2) bond. This easier interconversion in THF rather than in toluene is consistent with the higher basicity of THF, which can coordinate with the hard Sm(III) centre, thus liberating a coordination site so that the fluxional equilibrium of the pentadienyl ligand can occur readily.

However, we cannot decide whether the C_7H_{11} in **1**, or even in the structurally characterized $[Sm(\eta^8\text{-}C_8H_8)(\eta^5\text{-}C_7H_{11})(THF)]$ [4], is η^5 coordinated in solution since the symmetry observed in the ^1H NMR spectrum would also be compatible with a low energy fluxional process involving an equilibrium between structures in which a C_7H_{11} would be η^3 coordinated as in $[(C_7H_{11})_3Lu]$ [7].

The reaction of $YbCl_3$ with 3 equivalent of $[K(C_7H_{11})]$ in THF afforded a red precipitate. Extraction of this precipitate with 1,2-dimethoxyethane (DME) afforded a low yield of red crystals. The NMR spectrum of these crystals showed chemical shifts in the diamagnetic region and therefore that $YbCl_3$ had been reduced to yield a Yb(II) complex. The ^1H NMR spectrum indicated that this complex had the composition $[Yb(C_7H_{11})_2(DME)]$ (**2**). The same compound was obtained with a much better yield (60%) from 1 equivalent of YbI_2 and 2 equivalents of $[K(C_7H_{11})]$, see eqn. (3).



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(3)

The ^1H and ^{13}C NMR spectra of **2** are similar to, but significantly different from those of $[K(C_7H_{11})]$, the most important differences being the upfield shift of the C(1,5)atoms ($\Delta\delta = -10$ ppm) and the low field shift of the H(3) proton ($\Delta\delta = 0.5$ ppm) in the complex. Careful examination of the ^{13}C spectrum of **2** showed that the resonances of C(1,5) C(3) were flanked by satellites. The frequency separation between the two satellite lines remained the same at different field strengths.

Since we have already showed the presence of ^{171}Yb satellites in the ^{31}P NMR spectrum of π-phospholyl ytterbium(II) complexes [8], we believe that these satellites must arise from spin–spin coupling between the carbon atoms of the π-pentadienyl ligand and the ^{171}Yb nucleus. These coupling constants are $^1J_{C(1,5)-Yb} = 29.5$ Hz and $^1J_{C(3)-Yb} \approx 7$ Hz (Fig. 1). No satellites were observed in the C(2,4) signal but a small unresolved $^1J_{C(2,4)-Yb}$ coupling might contribute to the observed line broadening at the base. ^{171}Yb satellites were also found for the η^5-Cp* ring carbon atoms in the spectrum of $[Cp^*_2Yb(THF)_2]$ [9] * with a $^1J_{Cp^*-Yb}$ coupling constant of about 13 Hz. To our knowledge, these are the first reported ^{13}C–^{171}Yb spin–spin coupling constants. The presence of these satellites indicates that, if ligand exchange occurs in $[(C_7H_{11})_2Yb(DME)]$ or $[Cp^*_2Yb(THF)_2]$, it must be slow on the NMR time scale at room temperature. There are no obvious reasons for the differences between the $^1J_{Yb-C}$ coupling constants in **2**. Resolved coupling is observed only for those ligand carbonations (C(1), C(3) and C(5)) which bear a formal negative charge, or a non-zero coefficient in the highest occupied molecular orbital of the C_7H_{11} anion.

TABLE 1. X-ray experimental data

Empirical formula	$C_{18}H_{32}O_2Yb$
Formula weight	453.49
Space group	$P2_1/n$ (non-standard no. 14)
a (Å)	8.671(1)
b (Å)	14.721(1)
c (Å)	15.204(2)
β (°)	97.74(1)
V (Å^3)	1923.09(65)
Z	4
Crystal size (mm)	0.12×0.25×0.30
ρ_{calc} (g cm^{-3})	1.568
Linear absorption coefficient μ (cm^{-1})	48.6
Absorption correction	Empirical (DIFABS)
Radiation	Mo Kα (λ = 0.71073 Å)
Monochromator	Graphite
Maximum 2θ (°)	60
Number of reflections measured	6142 total, 5587 unique
Reflections included	4197 with $F_o^2 > 3.0\sigma(F_o^2)$
Unweighted agreement factor	0.035
Weighted agreement factor	0.050
Goodness of fit	1.05
Convergence, largest shift or error	0.01
Minimization function	$w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least-squares weights	$4F_o^2/\sigma^2 - (F_o^2)$, with $\sigma^2(F^2) = \sigma^2(I) + (pF^2)^2$
p factor	0.08

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* Reference number with asterisk indicates a note in the list of references.

3. Crystal and molecular structure of $[(C_7H_{11})_2Yb(DME)]$ (2)

We though that it could be interesting to compare the structure of **2** with that of the closely related bridged pentadienyl dimer $[\{\eta^5\text{-}4,4'\text{-}(CH_2)_2(2\text{-}C_6H_8)_2\}Yb(THF)_2]$ (**3**). Crystals of $[(C_7H_{11})_2Yb(DME)]$, were obtained from toluene. Crystal data and data collection parameters are listed in Table 1. Table 2 gives selected bond lengths and angles, and Fig. 2 shows an ORTEP plot for **2**. The Yb atom is coordinated to two $\eta^5\text{-}C_7H_{11}$ and a DME molecule through the oxygen atoms. The C_5H_{11} ligands are planar but not parallel, the dihedral angle being 31.3(4)°. This is much less than that has been found for Ernst's bridged compound **3** (50.6(4)°), which reflects the ring strain in this compound. On the average, the Yb–C bond lengths (2.75 Å) are intermediate between that of **3** (2.80 Å) and that of $[Cp_2Yb(DME)]$ [10] (2.72 Å), whereas the Yb–O lengths and the O–Yb–O angles have similar values to those in $[Cp_2Yb(DME)]$. The Yb–C bond lengths show a similar trend to that observed for **3** and also for the recently reported $[Yb(\eta^5\text{-}1,5\text{-}(Me_3Si)_2C_5H_5)(\eta^3\text{-}(Me_3Si)_2C_5H_5)(diglyme)]$ [3]: Yb–C(1,5) (2.79 Å) > Yb–C(2,3) (2.74 Å) > Yb–C(3) (2.69 Å).

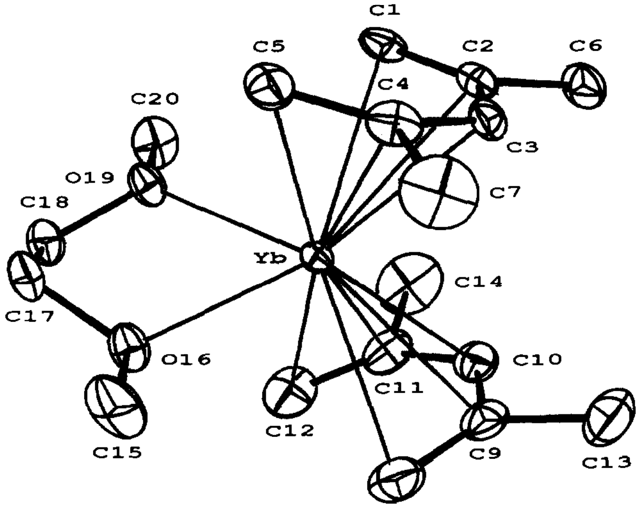

Fig. 2. An ORTEP plot of one molecule of $[(C_7H_{11})_2Yb(DME)]$ (2) Ellipsoids are scaled to enclose 50% of the overall electronic density.

4. Preliminary chemical studies on $[Sm(C_7H_{11})_3]$ and $[Nd(C_7H_{11})_3]$

We were interested in isolating cationic compounds, because of the potential usefulness of early-transition-metal complexes in Ziegler–Natta catalysis [11], and because few such compounds exist in lanthanoid chemistry [12]. Thus interaction of **1** with 1 equivalent of $[NEt_3][BPh_4]$ in THF resulted in immediate precipitation of a violet crystalline solid. Elemental C,H analysis is consistent with a composition $[(C_7H_{11})_2Sm(BPh_4)]$, but unfortunately this compound is completely insoluble in all organic solvents. When a similar reaction was performed with $[Nd(C_7H_{11})_3]$ (synthesized according to Ernst's method [5], a product that we formulate as $[(C_7H_{11})_2Nd(BPh_4)]$, according to the ^1H NMR spectrum was obtained as fine yellow needles with a 90% yield. The resonances of H(*endo*) and H(*exo*) are found at very high fields (−24.3 and −37.6 ppm), significant different from three of the starting material. However, no meaningful elemental analysis could be obtained.

TABLE 2. Selected bond lengths (Å) and angles (°)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Yb	C(1)	2.752(5)	Yb	C(8)	2.764(6)
Yb	C(2)	2.749(5)	Yb	C(9)	2.734(5)
Yb	C(3)	2.704(5)	Yb	C(10)	2.676(5)
Yb	C(4)	2.755(5)	Yb	C(11)	2.727(5)
Yb	C(5)	2.826(5)	Yb	C(12)	2.813(6)
Yb	O(16)	2.507(3)	Yb	O(19)	2.467(3)
C(1)	C(2)	1.368(7)	C(8)	C(9)	1.381(9)
C(2)	C(3)	1.427(7)	C(9)	C(10)	1.404(9)
C(3)	C(4)	1.414(7)	C(10)	C(11)	1.442(8)
C(4)	C(5)	1.366(8)	C(11)	C(12)	1.360(10)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C(1)	C(2)	C(3)	128.2(5)	C(8)	C(9)	C(10)	128.6(5)
C(2)	C(3)	C(4)	129.4(4)	C(9)	C(10)	C(11)	129.2(5)
C(3)	C(4)	C(5)	129.1(5)	C(10)	C(11)	C(12)	128.2(6)
O(16)	Yb	O(19)	66.5(1)				

5. Experimental section

5.1. *General*

All operations were performed under an inert atmosphere using a high vacuum line and dry-box techniques. All solvent were carefully dried and deoxygenated. NMR spectra were obtained on Bruker WP80, AC 200 and AM 400 spectrometer chemical shifts are referred in δ units from internal tetramethylsilane (^{13}C or ^1H). Elemental analyses were obtained from Analytische Laboratorien, Engelskirchen, Germany, and from Service de Microanalyse du CNRS, Gif-sur-Yvette, France, $[K(C_7H_{11})]$ [13], $[Nd(C_7H_{11})_3]$ [5], $[YbI_2(THF)_2]$ [14] and $[NEt_3H][BPh_4]$ [15] were prepared as previously described. All reagents were used as received from the commercial suppliers.

5.2. *$[Sm(C_7H_{11})_3]$ (1)*

To a solution of $SmCl_3$ (130 mg, 0.51 mmol) in THF (15 ml) was added $[K(C_7H_{11})]$ (200 mg, 1.49 mmol).

e resulting pink solution was filtered and evaporated dryness. The pink residue was recrystallized from uene, filtered and dried, yielding **1** (100 mg, 0.23 nol; 45%) as pink crystals.

^{1}H NMR (C_7D_8, 303 K): δ 1.17 (s, 6H, CH_3), 3.38 2H, H(*endo*) or H(*exo*)), 12.36 (s, 2H, H(*endo*) or *exo*)), 14.95 (s, H_3). Anal. Found: C, 57.17; H, 7.52. $_{1}H_{33}$Sm calc.: C, 57.87; H, 7.63%.

3. *[Sm(η^8-C_8H_8)(η^5-C_7H_{11})(THF)]*

This was prepared according to ref. 4.

^{1}H NMR (C_4D_8O, 303 K): δ – 1.85 (s, 2H, H(*endo*) H(*exo*)), 3.25 (s, 6H, CH_3), 5.17 (s, 2H, H(*endo*) or (*exo*)), 11.52 (s, 8H, C_8H_8), 14.54 (s, 1H. H_3).

4. *[(C_7H_{11})$_2$Yb(DME)] (2)*

5.4.1. *Method 1*

To a suspension of $YbCl_3$ (280 mg, 1 mmol) in THF 0 ml) was added [K(C_7H_{11})] (400 mg, 2.98 mmol). he reaction mixture turned dark red. The dark-red recipitate was filtered and extracted into DME. The sulting solution was evaporated to dryness and the sidue dissolved in toluene, and filtered. On evaporatng to dryness, red crystals of **2** were deposited. They ere washed with cold hexane and dried (90 mg, 0.20 mol; 20%).

5.4.2. *Method 2*

A solution of [$YbI_2(THF)_2$] (1.42g, 2 mmol) and K(C_7H_{11})] (537 mg, 4 mmol) in DME (25 ml) was tirred for 1 h at room temperature and then evapoated to dryness *in vacuo*. The residue was extracted nto toluene, filtered and evaporated to dryness. The esulting crystals were extracted into hexane, and this olution was filtered and evaporated to dryness. The esidue was thoroughly pumped or a vacuum line (570 ng, 1.28 mmol; 64%). ^{1}H NMR (C_4D_8O): δ 1.79 (s, H, CH_3–C_2), 3.20 (br. s, 2H, H(*endo*)), 3.31 (s, 3H, H$_3$ (DME)), 3.46 (s, 2H, CH_2 (DME)), 3.54 (br. s, H, H exo), 3.71 (t, $J = 2$ Hz, 1H, H_3). ^{13}C{^{1}H} NMR: 28.66 (CH_3), 59.34 (CH_3 (DME)), 72.55 (CH_2 DME)), 77.57 (C_1) 87.00 (C_3), 145.12 (C_2). See main ext for a discussion about the satellites.

5.5. *Reaction of [Sm(C_7H_{11})$_3$] with [NEt_3H][BPh_4]*

A mixture of [NEt_3H][BPh_4] (50 mg, 0.12 mmol) and [Sm(C_7H_{11})$_3$] (50 mg, 0.11 mmol) in THF (5 ml) was stirred at room temperature. Violet crystals soon appeared in a red–violet solution. These crystals were filtered, washed with THF and dried *in vacuo*. 45 mg of [(C_7H_{11})$_2$Sm(BPh_4)] were obtained (0.07 mmol; 57%).

Anal. Found: C, 68.89, H, 6.40. $C_{38}H_{42}BSm$, C, calc.: 69.16; H, 6.41%.

5.6. *Reaction of [Nd(C_7H_{11})$_3$] with [NEt_3H][BPh_4]*

A solution of [Nd(C_7H_{11})$_3$] (55 mg, 0.13 mmol) and [NEt_3H][BPh_4] (50 mg, 0.12 mmol) in THF (15 ml) was stirred for 15 mn. The greenish-yellow reaction mixture was then concentrated and fine yellow needles of [(C_7H_{11})$_2$Nd(BPh_4)] appeared on adding pentane. These needles were filtered, washed with pentane and dried (70 mg, 0.11 mmol; 90%).

NMR (C_4D_8O): δ –37.65 (br.s, 2H, H(*endo*) or H(*exo*)), –24.29 (br.s., H(*endo*) or H(*exo*)), 6.66, 7.19 (d, 20H, C_6H_5), 7.57 (s, 6H, CH_3), 18.35 (s, 1H, H_3).

5.7. *X-ray structure determination for 2*

Crystals of $C_{18}H_{32}O_2Yb$ (**2**) were grown from a toluene solution. Data were collected with an Enraf–Nonius CAD4 diffractometer. The crystal structure was solved and refined using the Enraf–Nonius MOLEN package. The ytterbium atom was located on a Patterson map, and the models were completed by successive difference Fourier maps. An empirical absorption correction was performed (DIFABS). The hydrogen atoms were included in the final stages of the refinement, as riding atoms with fixed $B_{iso} = 1.3$ times that of the attached C atom, while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor of 0.08. The final agreement factors were $R = 0.035$, $R_w = 0.050$. X ray data will be deposited at the Cambridge Crystallographic Data Centre.

Acknowledgments

The financial support of CEA, CNRS and Ecole Polytechnique is gratefully acknowledged.

References and notes

1 For a recent review, see R.D. Ernst, *Chem. Rev.*, *88* (1988) 1255.

2 W.-Q. Weng, K. Kunze, A.M. Arif and R.D. Ernst, *Organometallics*, *10* (1991) 3643.

3 K. Kunze and R.D. Ernst, *Bull. Soc. Chim. Fr.*, *130* (1993) 708.

4 J. Jin, S. Jin, Z. Jin and W. Chen, *J. Chem. Soc., Chem. Commun.*, (1991) 1328.

5 R.D. Ernst and T.H. Cymbaluk, *Organometallics*, *1* (1982) 708.

6 J. Sieler, A. Simon, K. Peters, R. Taube and M. Geitner, *J. Organomet. Chem*, *362* (1989) 297.

7 H. Schumann and A. Dietrich, *J. Organomet. Chem*, *401* (1991) C33.

8 F. Nief, L. Ricard and F. Mathey, *Polyhedron*, *12* (1993) 19.

9 Prepared from [$YbI_2(THF)_2$] and KCp* according to ref. 14a.

10 G.B. Deacon, P.I. McKinnon, T.W. Hambley and J.C. Taylor, *J. Organomet. Chem.*, *259* (1983) 91.

11 J.J. Eisch, A.M. Piotrowski, S.K. Brownstein, E.J. Gabe and F.L. Lee, *J. Am. Chem. Soc.*, *107* (1985) 4127; R.F. Jordan, C.S. Bajgur, R.W. Willett and B.S. Scott, *J. Am. Chem. Soc.*, *108* (1986) 7410; Z. Lin, J.F. Le Marechal, M. Sabat and T.J. Marks, *J. Am. Chem. Soc.*, *109* (1987) 4127; J.J.W. Eehuis, Y.Y. Tan, J.H.

Teuben and J. Renkema, *J. Mol. Catal.*, *62* (1990) 277; P.N. Hazin, J.W. Bruno and G.K. Schulte, *Organometallics*, *9* (1990) 2124; H.J. Heeres, A. Meetsma and J.H. Teuben, *Organomet. Chem.*, *414* (1990) 351; C.J. Schavieren, *Organometallics*, *11* (1992) 3476.

12 W.J. Evans, T.A. Ulibarri, L.R. Chamberlain, J.W. Ziller and D. Alvarez, Jr., *Organometallics*, *9* (1990) 2124.

13 H. Yasuda, Y. Ohnuma, M. Yamauchi, H. Tani and A. Nakamura, *Bull. Soc. Chim. Jpn.*, *52* (1979) 2036.

14 (a) P.L. Watson, T.H. Tulip and I. Williams, *Organometallics*, *9* (1990) 1999;
(b) J.-L. Namy, P. Girard, H.B. Kagan and P.E. Caro, *Nouv. J. Chim.*, *5* (1981) 479.

15 B.J. Barker and P.J. Sears, *J. Phys. Chem.*, *78* (1974) 2687.