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**Activation of sp<sup>3</sup>-CH Bonds in a Mono(pentamethylcyclopentadienyl)yttrium Complex. X-ray Crystal Structures and Dynamic Behavior of Cp\*Y(o-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub> and Cp\*Y[o-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe(CH<sub>2</sub>-μ)][μ-o-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe(CH<sub>2</sub>-μ)]Y Cp\*[THF]**

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*Published in:*  
 Organometallics

*DOI:*  
[10.1021/om00112a029](https://doi.org/10.1021/om00112a029)

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*Document Version*  
 Publisher's PDF, also known as Version of record

*Publication date:*  
 1989

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Booij, M., Kiers, N. H., Meetsma, A., Teuben, J. H., Smeets, W. J. J., & Spek, A. L. (1989). Activation of sp<sup>3</sup>-CH Bonds in a Mono(pentamethylcyclopentadienyl)yttrium Complex. X-ray Crystal Structures and Dynamic Behavior of Cp\*Y(o-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub> and Cp\*Y[o-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe(CH<sub>2</sub>-μ)][μ-o-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe(CH<sub>2</sub>-μ)]Y Cp\*[THF]. *Organometallics*, 8(10). DOI: 10.1021/om00112a029

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**Activation of  $sp^3$ -CH Bonds in a  
Mono(pentamethylcyclopentadienyl)yttrium Complex. X-ray  
Crystal Structures and Dynamic Behavior of  
 $Cp^*Y(o-C_6H_4CH_2NMe_2)_2$  and  
 $Cp^*Y[o-C_6H_4CH_2NMe(CH_2-\mu)][\mu-o-C_6H_4CH_2NMe(CH_2-\mu)]Y Cp^* -$   
 $[THF]^1$**

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Received March 2, 1989

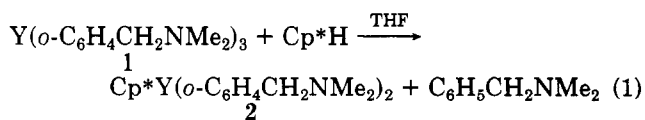
Reaction of  $Y(o-C_6H_4CH_2NMe_2)_3$  (1) with  $Cp^*H^1$  gives  $Cp^*Y(o-C_6H_4CH_2NMe_2)_2$  (2), which crystallizes in the monoclinic space group  $P2_1/n$  (No. 14) with  $a = 18.607$  (4) Å,  $b = 15.633$  (3) Å,  $c = 8.861$  (3) Å,  $\beta = 102.73$  (3)°, and  $Z = 4$ . Least-squares refinement with 3006 independent reflections ( $F > 4.0\sigma(F)$ ) led to a final  $R_F$  (wR) of 0.053 (0.068). The molecular structure consists of monomeric  $Cp^*Y(o-C_6H_4CH_2NMe_2)_2$  units with a regularly bonded  $Cp^*$  ligand ( $Y-Ct^1 = 2.367$  (3) Å), equal  $Y-C$  (aryl) distances (2.479 (6) and 2.471 (6) Å), and both nitrogen atoms coordinated to yttrium ( $Y-N$  distances = 2.568 (5) and 2.506 (6) Å). Short intramolecular  $Y\cdots H$  distances ( $Y\cdots H(181) = 3.00$  (6) Å,  $Y\cdots H(183) = 3.13$  (9) Å) indicate agostic interactions. The long  $N(2)-C(18)$  bond (1.55 (1) Å) and the short  $Y\cdots C(18)$  distance (3.202 (8) Å) indicate an  $Y\cdots C-N$  agostic interaction. Thermolysis of 2 in THF gives  $Cp^*Y[o-C_6H_4CH_2NMe(CH_2-\mu)][\mu-o-C_6H_4CH_2NMe(CH_2-\mu)]Y Cp^* [THF]$  (3) and  $N,N$ -dimethylbenzylamine. Compound 3 crystallizes in the monoclinic space group  $P2_1/c$  (No. 14) with  $a = 17.004$  (1) Å,  $b = 13.962$  (1) Å,  $c = 20.129$  (3) Å,  $\beta = 92.94$  (1)°, and  $Z = 4$ . Least-squares refinement with 4578 independent reflections ( $F > 5.0\sigma(F)$ ) led to a final  $R_F$  (wR) of 0.065 (0.070). The molecule consists of two  $Cp^*Y$  fragments ( $Y(1)-Ct(1) = 2.420$  (6) Å,  $Y(2)-Ct(2) = 2.414$  (5) Å), bridged by two methylene carbon atoms ( $Y(1)-C(9) = 2.591$  (10) Å,  $Y(2)-C(9) = 2.527$  (9) Å,  $Y(1)-C(18) = 2.622$  (10) Å,  $Y(2)-C(18) = 2.532$  (10) Å) and one aryl carbon atom ( $Y(1)-C(1) = 2.702$  (8) Å,  $Y(2)-C(1) = 2.547$  (9) Å). The remaining aryl group is not bridging ( $Y(1)-C(10) = 2.441$  (8) Å). Asymmetry in 3 is caused by THF coordination ( $Y(2)-O = 2.446$  (5) Å). Thermolysis of 2 can be explained by dissociation of an  $Y-N$  dative bond followed by activation of an agostic  $C-H$  bond.

### Introduction

Recently we started research on monopentamethylcyclopentadienyl complexes of group 3 elements and early lanthanides.<sup>2</sup> Unlike compounds of the  $Cp^*_2LnR$  type the number of well-defined mono- $Cp^*$  complexes of lanthanoid<sup>1</sup> elements is limited.<sup>2,3</sup> A clear reason is that in general mono- $Cp^*$  complexes are sterically less saturated than bis- $Cp^*$  complexes and a stable configuration is more difficult to achieve. It is not surprising that the undesirable incorporation of salt and solvent molecules, which is often observed in bis- $Cp^*$  complexes,<sup>4</sup> is found with

mono- $Cp^*$  complexes even more frequently.<sup>2c,3</sup> Although they are not readily accessible so far, these complexes form a challenging class. Two reactive bonds (e.g.  $Ln-C$ ,  $Ln-H$ ,  $Ln-N$ ,  $Ln-O$ , etc.) adjacent to a lanthanoid metal may display a reactivity totally different from that observed in the  $Cp^*_2LnR$  system.

One of our first successful attempts to enter this field has been the synthesis of a  $Cp^*YR_2$  complex. It appeared that salt incorporation could be circumvented by reacting a neutral homoleptic complex  $Y(o-C_6H_4CH_2NMe_2)_3$  (1), containing chelating amine functions, with  $Cp^*H$  (eq 1).<sup>2c</sup> In this way we obtained  $Cp^*Y(o-C_6H_4CH_2NMe_2)_2$  (2), which proved to be useful for further study.



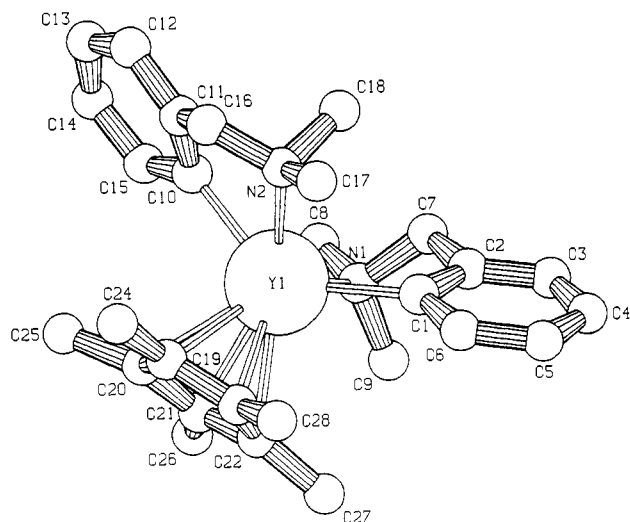
Since very little is known on the stability of the metal-carbon bond in mono- $Cp^*$  lanthanoid complexes,<sup>5</sup> we decided to investigate the thermal behavior of 2. It appeared that a  $C-H$  bond of the  $N-CH_3$  group of the chelating amine is thermally activated on heating 2 in THF. In the following we focus on the structural properties and the dynamic behavior of 2 and its thermolysis product.

(1) In this paper the following abbreviations are used:  $Cp = C_5H_5$ ,  $Cp^* = C_5H_4Me$ ,  $Cp^* = C_5Me_5$ ,  $Ln =$  lanthanoid (group 3 or 4f) element,  $Ct = Cp^*$  ring centroid.

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(5) (a) Thermal decomposition of  $Cp^*Ln[CH(SiMe_3)_2]_2$  gives  $CH_2(SiMe_3)_2$  and a so far unidentified organometallics product ( $Ln = La,^{6b} Ce^*$ ). (b) Heijden, H. J. van der; Schaverien, C. J.; Orpen, A. G. *Organometallics* 1989, 8, 255.



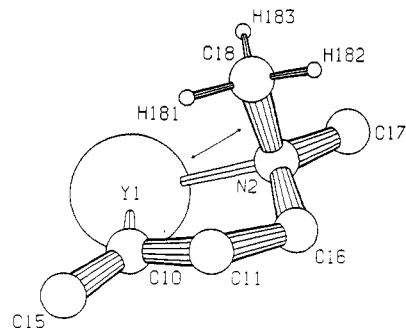
**Figure 1.** PLUTO drawing of  $Cp^*Y(o-C_6H_4CH_2NMe_2)_2$  (**2**) with the adopted numbering scheme (hydrogen atoms omitted for clarity).

**Table I.** Selected Distances (Å) and Angles (deg) for **2** with Estimated Standard Deviation Given in Parentheses in Units of the Least Significant Digit

a. Distances			
Y-Ct	2.367 (3)	Y-C(1)	2.479 (6)
Y-C(19)	2.673 (6)	Y-C(10)	2.471 (6)
Y-C(20)	2.658 (6)	Y-N(1)	2.568 (5)
Y-C(21)	2.645 (6)	N(1)-C(7)	1.497 (8)
Y-C(22)	2.642 (6)	N(1)-C(8)	1.472 (8)
Y-C(23)	2.657 (6)	N(1)-C(9)	1.465 (8)
Y-C(ring) <sub>av</sub>	2.655 (8)	Y-N(2)	2.506 (6)
Cp*(C-C) <sub>int,av</sub>	1.42 (6)	N(2)-C(16)	1.47 (1)
Cp*(C-C) <sub>ext,av</sub>	1.51 (1)	N(2)-C(17)	1.441 (9)
		N(2)-C(18)	1.55 (1)
b. Angles			
Y-C(1)-C(2)	111.9 (4)	Y-C(10)-C(11)	113.9 (5)
C(1)-C(2)-C(7)	117.8 (5)	C(10)-C(11)-C(16)	121.7 (8)
C(2)-C(7)-N(1)	111.6 (5)	C(11)-C(16)-N(2)	108.7 (7)
C(7)-N(1)-C(8)	108.9 (4)	C(16)-N(2)-C(17)	116.6 (6)
C(7)-N(1)-C(9)	107.8 (5)	C(16)-N(2)-C(18)	103.8 (7)
C(7)-N(1)-Y	100.2 (3)	C(16)-N(2)-Y	109.8 (5)
C(8)-N(1)-Y	113.9 (4)	C(17)-N(2)-Y	117.1 (4)
C(9)-N(1)-Y	117.1 (3)	C(18)-N(2)-Y	101.6 (4)

## Results and Discussion

**a. Molecular Structure of 2.** Compound **2** is a 14-electron system and thus very electron-deficient. To relieve the electronic and coordinative unsaturation these complexes often have bridging ligands<sup>6</sup> and display agostic<sup>7</sup> interactions.<sup>2a,6d,8</sup> Therefore we thought it relevant to determine the molecular structure of **2** by X-ray diffraction. The compound crystallizes from pentane in the monoclinic space group  $P2_1/n$  with four monomeric



**Figure 2.** PLUTO drawing of the Y...C-N agostic interaction in **2**.

molecules of **2** in the unit cell. At first sight the  $Cp^*$  and the two *o*-[(dimethylamino)methyl]phenyl ligands are bonded in a normal way. The  $Cp^*$  ring is dish-shaped (average displacement from the ring plane of the methyl groups = 0.11 Å, directed away from the metal<sup>9</sup>) and regularly  $\eta^5$ -bonded to yttrium. The average Y-C(ring) and Y-Ct distances of 2.655 (8) (range 2.642 (6) to 2.673 (6) Å) and 2.367 (3) Å, respectively (Table I), are close to those found in  $Cp^*_2YR$  complexes ( $R = CH(SiMe_3)_2$ ,<sup>8a</sup>  $N(SiMe_3)_2$ ,<sup>8a</sup>  $Cl\cdot THF$ <sup>10</sup>). The average internal and external C-C distances in the  $Cp^*$  ring (1.42 (1) and 1.51 (1) Å) are within the usual range. The *o*-[(dimethylamino)methyl]phenyl ligands each form a five-membered metallocyclic ring, with the metal and three carbon atoms virtually coplanar (deviations within 0.01 Å) and the  $NMe_2$  groups out of the plane ( $N1$ , 0.91 (1);  $N2$ , 0.66 (2) Å). The torsion angles  $C(1)-C(2)-C(7)-N(1)$  and  $C(20)-C(21)-C(26)-N(2)$  are  $-45.6$  (7)° and  $37$  (1)°, respectively, comparable with those found in the related compounds  $Cp_2Y-o-C_6H_4CH_2Me_2$ <sup>11</sup> ( $32.2^\circ$  and  $-34.1^\circ$ ) and  $Lu(o-C_6H_4CH_2NMe_2)_3$ <sup>12</sup> ( $-25^\circ$ ,  $31^\circ$ ,  $-38^\circ$ ), but representing rather extreme values. The geometry of the metallocycles is normal. Corresponding bonds and angles are equal within error limits, but the Y-N bond and one of the N-C(Me) bonds,  $N(2)-C(18)$ , deviate. The yttrium-phenyl carbon distances Y-C(1) (2.479 (6) Å) and Y-C(10) (2.471 (6) Å) are equal. They are a bit longer than in  $Cp_2Y-o-C_6H_4CH_2NMe_2$ <sup>11</sup> although the large estimated standard deviations in the latter structure make a detailed comparison of these yttrium chelates difficult. The Y-C distance in bis(pentamethylcyclopentadienyl) alkyls  $Cp^*_2YCH(SiMe_3)_2$ <sup>8a</sup> and  $Cp^*_2YCH_3\cdot THF$ <sup>13</sup> (2.468 (7) and 2.44 (2) Å) are very similar, thus indicating that normal Y-C bonds can be expected to be about 2.47 Å. The dative bonds between the dimethylamino function and yttrium differ significantly ( $Y-N(1) = 2.568$  (5) Å,  $Y-N(2) = 2.506$  (6) Å) and indicate secondary interactions between the metal and the [(dimethylamino)methyl]phenyl ligand with the shorter Y-N bond. Inspection of the intramolecular distance shows that this is indeed the case. Two Y-H contacts ( $Y-H(181) = 3.00$  (6) Å and  $Y-H(183) = 3.13$  (9) Å) and one Y-C distance ( $Y-C(18) = 3.202$  (8) Å) are significantly shorter than the sum of the van der Waals

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radii.<sup>14</sup> Five of the six C-N bonds are within the normal range (1.47 Å) for a C-N single bond,<sup>15</sup> but C(18)-N(2) (1.55 (1) Å) is dramatically longer. Furthermore, the Y-N(2)-C(18) angle (101.5 (4)°) is much smaller than the Y-N(2)-C(16) (109.9 (5)°) and Y-N(2)-C(17) (117.1 (4)°) angles (Figure 2). These features indicate an Y...C-N agostic interaction, similar to the Ti...C-Si agostic interaction recently reported for Cp<sub>2</sub>TiC(SiMe<sub>3</sub>)=C(Me)(Ph)<sup>+</sup>.<sup>16</sup> Considering the MO scheme for a four-legged piano-stool complex of the type CpML<sub>4</sub>, the LUMO on yttrium (d<sub>z<sup>2</sup></sub>) has the proper orientation for this interaction.<sup>17</sup> It is the first observation of a C-N agostic interaction to our knowledge. Whether the observed Y...C(18)-N(2) interaction is the only secondary interaction in **2** cannot be decided with certainty. A neutron diffraction study will be necessary to decide whether the short distances Y-H(181) and Y-H(183) are due to agostic Y...H-C bonds or whether they are forced into this position by the interaction with the C-N bond electrons. It is clear from the structure of **2** that other potential sites for agostic C-C or C-H bonds (i.e. around C(7), C(8), C(17)) are not used.

One final comment on the difference in Y-N bonds can be made here. Similar differences have been found in Cp<sub>2</sub>Y-*o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub><sup>11</sup> (two independent molecules in the asymmetric unit) display Y-N distances of 2.43 (2) and 2.54 (2) Å and in Lu(*o*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>)<sub>3</sub><sup>12</sup> (Lu-N bonds of 2.468 (6), 2.478 (5), and 2.588 (5) Å). In both a short Y-N and long N-C(Me) (1.58 (4) Å) suggest an agostic Y...C-N bond, but the long Y-C distance (3.48 Å vs 3.202 (8) Å in **2**) seems to be in contradiction. In the homoleptic compound Lu(*o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>3</sub>, two short (2.468 (6) and 2.478 (5) Å) and one long (2.588 (5) Å) Y-N bonds are found. However, the six C-N bonds are normal (1.46 (1)-1.50 (1) Å). The structure shows two short Lu-C contacts (Lu-C(8) = 3.187 (7) Å and Lu-C(26) = 3.20(1) Å). Since these do not correspond with a long C-N bond at the same amine function, it is more likely that in Lu(*o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>3</sub> agostic Lu...C-H bonds are present than are Lu...N-C interactions.

**b. Dynamic Behavior of 2 in Solution.** At room temperature, <sup>1</sup>H and <sup>13</sup>C NMR (toluene-*d*<sub>6</sub>/TMS)<sup>2c</sup> show equivalent *o*-[(dimethylamino)methyl]phenyl groups. This indicates that in solution the agostic interactions are absent or interchanging between the two *o*-[(dimethylamino)methyl]phenyl ligands. This process has a very low activation barrier because the system is still fluxional at -90 °C.<sup>18</sup> The two <sup>1</sup>H NMR resonances for the diastereotopic N-CH<sub>3</sub> groups (δ 2.04 and 1.99 ppm) coalesce at 115 °C giving Δ*G*<sup>‡</sup><sub>115°C</sub> = 84 (±2) kJ·mol<sup>-1</sup><sup>19</sup> for the exchange process. The observed dynamic behavior can be explained by dissociation of the Y-N donor bond, followed by rotation around the CH<sub>2</sub>-NMe<sub>2</sub> axis, inversion of configuration on nitrogen, and finally a recoordination of the amine.

**c. Thermolysis of 2.** Agostic interactions have been suggested as possible pre-transition states for C-H acti-

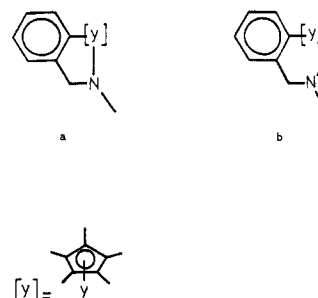


Figure 3. Possible reaction pathways for **2**.

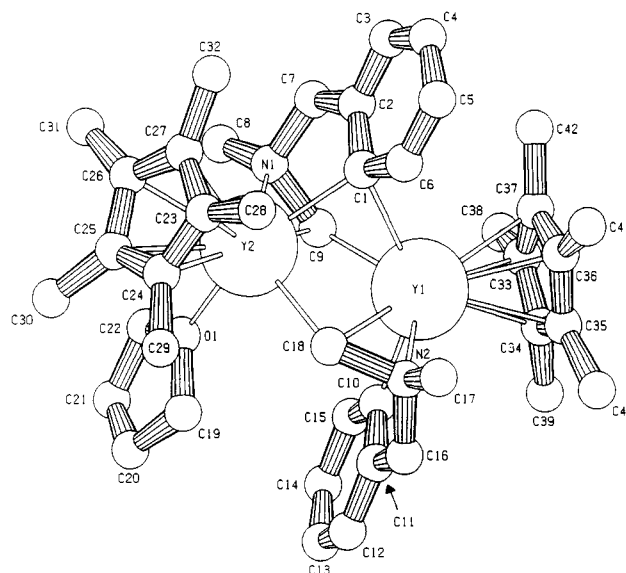
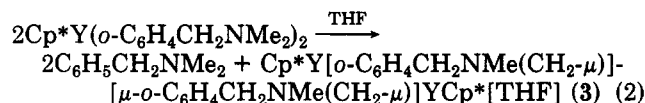


Figure 4. PLUTO drawing of Cp\*Y[*o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe(CH<sub>2</sub>-μ)] [μ-*o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe(CH<sub>2</sub>-μ)]Y Cp\*[THF] (**3**) with the adopted numbering scheme (hydrogen atoms omitted for clarity).

vation.<sup>20a</sup> Although agostic C-H<sup>7</sup> interactions<sup>2a,6d,8</sup> and C-H activation<sup>20</sup> have often been reported for d<sup>0</sup> systems, the activation of particular agostic C-H bonds has been observed less frequently<sup>20</sup> and the relation of C-H agostic interactions with activation processes is still subject to discussion.

Because **2** contained a unique Y...C-N as well as Y...C-H agostic interactions, we were interested to see which of these bonds could be thermally activated. Activation of an agostic C-H bond and a C-N bond in **2** can possibly give two reaction products (Figure 3): a five-membered ring with a direct Y-N bond (a) or a six-membered ring with two Y-C bonds (b).

On heating **2** in THF quantitative formation of 1 mol of *N,N*-dimethylbenzylamine/mol of yttrium was observed (NMR), which indicated that a C-H bond had been activated. The organoyttrium product proved to be exclusively a dinuclear complex, **4**, with bridging *o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe(CH<sub>2</sub>) ligands (eq 2). X-ray analysis of **3** gave detailed information on its structure and bonding.



**d. Molecular Structure of 3.** Complex **3** crystallizes from benzene in the monoclinic space group *P*2<sub>1</sub>/*c*. The

(14) (a) van der Waals radii: *r*<sub>H</sub> = 1.20 Å, *r*<sub>Y</sub> = 2.58 Å, and *r*<sub>C</sub> = 1.70 Å. Values are those given in ref 14b (or covalent radius +0.8 Å when not given). (b) Bondi, A. *J. Phys. Chem.* 1964, 68, 441.

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(18) <sup>13</sup>C NMR of **2** (-90 °C, toluene-*d*<sub>8</sub>, 75.4 MHz): δ 69.04 (t, <sup>1</sup>*J*<sub>CH</sub> = 134.7 Hz, N-CH<sub>2</sub>-C(aryl ring)), 45.78 (q, <sup>1</sup>*J*<sub>CH</sub> = 135.8 Hz, N-CH<sub>3</sub>).

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**Table II. Selected Distances (Å) and Angles (deg) for 3 with Estimated Standard Deviation Given in Parentheses in Units of the Least Significant Digit<sup>a</sup>**

a. Distances			
Y(1)-Ct(1)	2.420 (6)	Y(2)-Ct(2)	2.414 (5)
Y(1)-C(ring) <sub>av</sub>	2.69 (3)	Y(2)-C(ring) <sub>av</sub>	2.69 (2)
Y(1)-C(33)	2.71 (1)	Y(2)-C(23)	2.69 (1)
Y(1)-C(34)	2.72 (1)	Y(2)-C(24)	2.72 (1)
Y(1)-C(35)	2.69 (1)	Y(2)-C(25)	2.70 (1)
Y(1)-C(36)	2.65 (1)	Y(2)-C(26)	2.67 (1)
Y(1)-C(37)	2.66 (1)	Y(2)-C(27)	2.68 (1)
Cp*(1)(C-C) <sub>int,av</sub>	1.37 (2)	Cp*(2)(C-C) <sub>int,av</sub>	1.40 (2)
Cp*(1)(C-C) <sub>ext,av</sub>	1.50 (3)	Cp*(2)(C-C) <sub>ext,av</sub>	1.51 (1)
Y(1)-C(1)	2.702 (8)	Y(2)-C(1)	2.547 (9)
Y(1)-C(9)	2.591 (10)	Y(2)-C(9)	2.527 (9)
Y(1)-C(10)	2.441 (8)	Y(2)-O	2.446 (5)
Y(1)-C(18)	2.622 (10)	Y(2)-C(18)	2.532 (10)
Y(1)-N(2)	2.405 (6)	Y(2)-N(1)	2.403 (6)
N(2)-C(16)	1.482 (11)	N(1)-C(7)	1.479 (12)
N(2)-C(17)	1.469 (12)	N(1)-C(8)	1.475 (12)
N(2)-C(18)	1.502 (12)	N(1)-C(9)	1.483 (12)
b. Angles			
Y(1)-C(1)-Y(2)	77.6 (2)	C(1)-C(9)-C(18)	55.7 (3)
Y(1)-C(9)-Y(2)	80.0 (3)	C(9)-C(18)-C(1)	49.2 (2)
Y(1)-C(18)-Y(2)	79.3 (3)	C(18)-C(1)-C(9)	75.1 (3)
Y(1)-C(1)-C(2)	117.6 (6)	Y(1)-C(10)-C(11)	114.3 (6)
C(1)-C(2)-C(7)	121.5 (8)	C(10)-C(11)-C(16)	119.9 (8)
C(2)-C(7)-N(1)	117.3 (8)	C(11)-C(16)-N(2)	114.3 (8)
C(7)-N(1)-Y(2)	112.6 (5)	C(16)-N(2)-Y(1)	113.1 (5)
C(8)-N(1)-Y(2)	130.1 (5)	C(17)-N(2)-Y(1)	126.5 (5)
C(9)-N(1)-Y(2)	77.1 (4)	C(18)-N(2)-Y(1)	80.7 (5)

<sup>a</sup> Cp\*(1) = C33-C42; Cp\*(2) = C23-C32.

unit cell contains four discrete molecules of **3** and six benzene solvate molecules. The molecule (Figure 4) is a binuclear yttrium complex which is the net result of hydrogen abstraction from a N-CH<sub>3</sub> group of one *o*-[(dimethylamino)methyl]phenyl ligand by the other *o*-[(dimethylamino)methyl]phenyl ligand in **2**. The metal atoms are bridged by two *o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe(CH<sub>2</sub>) ligands, and coordination of a THF molecule on Y(2) introduces asymmetry. Similar to its precursor **2**, the Cp\* ligands are bonded in the usual dish-shaped η<sup>5</sup>-fashion (Table II). The Y(1)-C(ring) and Y(2)-C(ring) distances vary between 2.65 (1)-2.71 (1) Å and 2.67 (1)-2.72 (1) Å. The Y(1)-Ct(1) and Y(2)-Ct(2) distances of 2.420 (6) and 2.414 (5) Å, respectively, are somewhat longer than in **2**, but taking into account the difference in temperature at which the data collection was done, the significance is marginal. The average out of plane bending of the methyl groups is 0.15 (4) and 0.14 (3) Å, respectively.

The Cp\*Y fragments are kept together by three asymmetrically bridging carbon atoms: C(1)(aryl); C(9) and C(18) (both alkyl). The distances to Y(2) (Y(2)-C(1) = 2.547 (9) Å; Y(2)-C(9) = 2.527 (9) Å; Y(2)-C(18) = 2.53 (1) Å) are equal within error limits. To Y(1) the Y-C distances are significantly longer than those to Y(2), with the aryl bridge (Y(1)-C(1) = 2.702 (8) Å) slightly longer than the two alkyl bridges (Y(1)-C(9) = 2.59 (1) Å and Y(1)-C(18) = 2.62 (1) Å). In particular Y(1)-C(1) is quite long, but still within bonding range and comparable to the Y-C (Cp\* ring) distances. The bridging Y-C bonds to Y(2) are very well comparable to those found in other carbon bridged organoyttrium compounds [Cp<sub>2</sub>Y(μ-Me)<sub>2</sub>]<sub>2</sub><sup>6b</sup> and [Cp<sub>2</sub>Y(μ,η<sup>2</sup>-HC=NCMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub><sup>6f</sup>. The terminal metal-aryl-carbon bond Y(1)-C(10) has a normal value of 2.441 (8) Å.<sup>5a,13</sup> The Y-N distances Y(1)-N(2) (2.405 (6) Å) and Y(2)-N(1) (2.403 (6) Å) are significantly shorter than those in **2** but identical with the Y-N distance in Cp\*<sub>2</sub>Y[η<sup>2</sup>-C-(DMB)=N(2,6-xylyl)]·THF (DMB = 3,5-dimethylbenzyl).<sup>21a</sup> This seems to be a normal Y-N distance in

**Table III. <sup>13</sup>C NMR of 3 (Toluene-d<sub>8</sub>/TMS, 75.4 MHz)<sup>a</sup>**

atoms	-80 °C		60 °C
	C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub>	116.16 (s)	115.07 (s)
C <sub>6</sub> (CH <sub>3</sub> ) <sub>5</sub>	11.96 (q)	11.29 (q)	16.56 (q)
	124.3 <sup>b</sup>	124.3 <sup>b</sup>	124.9 <sup>b</sup>
N-CH <sub>3</sub>	52.02 (q)	50.06 (q)	56.84 (q)
	135.8 <sup>b</sup>	137.0 <sup>b</sup>	134.8 <sup>b</sup>
N-CH <sub>2</sub> -C(aryl)	72.18 (t)	68.71 (t)	76.37 (t)
	133.5 <sup>b</sup>	133.5 <sup>b</sup>	132.9 <sup>b</sup>
N-CH <sub>2</sub> -Y	65.30 (td)	60.80 (td)	70.04 (td)
	116.9 <sup>b</sup>	116.9 <sup>b</sup>	117.2 <sup>b</sup>
	34.5 <sup>c</sup>	19.6 <sup>c</sup>	28.4 <sup>c</sup>
Y-C(aryl)	193.72 (d)	175.15 (dd)	189.55 (s, br)
	46.0 <sup>c</sup>	23.0, <sup>c</sup> 11.5 <sup>c</sup>	...
α-C(THF)	69.54 (t)		75.01 (t)
	148.5		149.0
β-C(THF)	25.48 (t)		30.57 (t)
	133.5		134.2

<sup>a</sup> Chemical shifts in ppm (multiplicity). <sup>b</sup> <sup>1</sup>J<sub>CH</sub> in Hz. <sup>c</sup> <sup>1</sup>J<sub>CY</sub> in Hz.

η<sup>2</sup>-C,N-coordinated complexes. Both shorter (2.325 (4) Å in [Cp<sub>2</sub>Y(μ,η<sup>2</sup>-HC=NCMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub><sup>6f</sup>) and longer (2.54 (2) Å in Cp<sub>2</sub>Y-*o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sup>11</sup>) Y-N bonds have been reported. Finally, the Y(2)-O(1) dative bond of 2.446 (5) Å is comparable to those found in other THF containing yttrium complexes.<sup>13,21</sup>

The remarkable differences in Y(1)-C and Y(2)-C distances of the bridge is a puzzling feature of the structure of **3**. Were this asymmetry due to electronic effects—i.e. the presence of an electron-donating THF ligand on Y(2) or a terminal aryl group on Y(1)—then similar bond lengthening should be expected for the other ligands as well, resulting in longer Y(1)-C(Cp\* ring) and Y(1)-N(1) bonds. This clearly is not the case. Another reason for the difference in bond length, e.g. steric crowding on Y(2) because of the presence of the THF ligand, would result in longer Y(2)-C bonds, but the reverse is observed. Further studies on related complexes are needed before this difference can be understood.

Despite the high electron deficiency (**3** is a 26-electron complex) a second THF is not coordinated, so clearly the steric crowding of the metal centers in **3** is high. Instead, two extremely short Y...H distances (Y(1)...H(92) = 2.52 (7) Å, Y(2)...H(181) = 2.78(7) Å) and correspondingly small Y-C-H angles (Y(1)-C(9)-H(92) = 76 (4)°, Y(2)-C(18)-H(181) = 93 (4)°) are observed. These agostic interactions furnish additional electronic saturation for the complex. The distances Y(2)...H(91) and Y(2)...H(182) of 2.99 (7) and 2.82 (6) Å, respectively, are also short, but the corresponding Y(2)-C(9)-H(91) (107(4)°) and Y(2)-C(18)-H(182) (102 (5)°) angles fall within the tetrahedral range. Deformation of the molecular framework to allow an interaction of the metal atoms with the π-electron density of the *o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe(CH<sub>2</sub>) ligands is not favored. The aryl ring carbons are coplanar within 0.02 Å, and the average C-C distances are 1.391 (8) and 1.392 (9) Å.

**e. Dynamic Behavior of 3 in Solution.** Low-temperature <sup>13</sup>C NMR (Table III) shows a double set of signals for both the Cp\* and the *o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe(CH<sub>2</sub>) ligand. The terminal Y-C(aryl) appears as a doublet (<sup>1</sup>J<sub>CY</sub> = 46.0 Hz), and the bridging Y-C(aryl) appears as double doublet (<sup>1</sup>J<sub>CY</sub> = 23.0 and 11.5 Hz). Both multiplicity and <sup>1</sup>J<sub>CY</sub> values indicate that the asymmetrical, dinuclear solid-state

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structure is retained in solution.

Because both N-CH<sub>2</sub>-Y signals are observed as doublets with respect to yttrium (<sup>1</sup>J<sub>CY</sub> = 34.5 and 19.6 Hz), they might be terminally bonded, but this is not very likely. Values for <sup>1</sup>J<sub>CY</sub> lower than 30 Hz generally indicate bridging carbon atoms. Furthermore, in similarly carbon-bridged [Cp<sub>2</sub>Y(μ,η<sup>2</sup>-HC=NCMe<sub>3</sub>)<sub>2</sub>] and [Cp'<sub>2</sub>Y(μ,η<sup>2</sup>-HC=NCMe<sub>3</sub>)<sub>2</sub>], one of the <sup>1</sup>J<sub>CY</sub> coupling constants is very small (5.0 and 4.7 Hz, respectively).<sup>6f</sup> This may be caused by a very small s contribution<sup>22,23</sup> in the interaction of the bridging carbon with one of the two yttrium nuclei. The possibility of one bridging aryl ligand holding the complex together is very unlikely due to the extremely "naked" metal atoms that would result. The chemical shifts for the THF α-C and β-C indicate coordination to yttrium.

At 60 °C only one set of signals for both the Cp\* and the o-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe(CH<sub>2</sub>) ligand is observed. Because the dissociation of 3 into monomeric units is very unlikely, a dynamic process that interchanges the different ligand positions is expected. The Y-C(aryl) resonance is broad, and yttrium couplings are not observed.<sup>23</sup> The N-CH<sub>2</sub>-Y resonance shows an yttrium coupling that is the average of the two low-temperature values. This is consistent with the fast exchange of the terminal and bridging positions for the aryl carbons, the N-CH<sub>2</sub>-Y bridges remaining essentially the same. To explain the equivalence of the Cp\* ligands, the averaging process must also include migration of THF.

Variable-temperature <sup>1</sup>H NMR (-80 to +60 °C) gives additional information on this dynamic process. The spectrum at -80 °C also shows a double set of signals (ratio 1:1) for the Cp\* and the o-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe(CH<sub>2</sub>) ligands which is in accord with a dinuclear structure. The α-H-(THF) signals appear as two broad singlets (2.96 and 2.11 ppm), which can be explained by assuming hindered rotation around the Y-O axis. The coalescence of the α-H-(THF) (0 °C), C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub> (5 °C), N-CH<sub>3</sub> (10 °C), and N-CH<sub>2</sub>-C(aryl) (15 °C) signals gives an average ΔG<sup>‡</sup> of 56 (±2) kJ·mol<sup>-1</sup><sup>18</sup> for the dynamic process that makes the two different ligand sites equivalent.

This dynamic behavior can be explained by THF dissociation from 3, followed by recoordination of THF on the other side of the molecule, or by nondissociative migration of THF to the other side of the molecule. A similar THF exchange process with a ΔG<sup>‡</sup>,<sub>50°C</sub> of 54 kJ·mol<sup>-1</sup> has been reported for Cp\*<sub>2</sub>LuCl·THF.<sup>24</sup>

**f. Mechanism.** Thermolysis of 2 in deuterated solvents (THF, benzene, toluene) shows no H/D exchange under the reaction conditions while the conversion of 2 to 3 in THF is quantitative (NMR). Other d<sup>0</sup> systems that exhibit H/D exchange show a preference for the activation of C-H bonds with sp and sp<sup>2</sup> hybridization over sp<sup>3</sup>-hybridized C-H bonds and are generally not selective.

To explain the selective activation of sp<sup>3</sup> C-H bonds in 2, we assume that the conversion of 2 to 3 proceeds via an intramolecular pathway. <sup>1</sup>H NMR has shown (vide supra) that the chelating amine functions become fluxional at elevated temperatures. This process makes the metal center coordinatively more unsaturated and electron-deficient (Figure 5). This can lead to a stronger Y...N-C-H

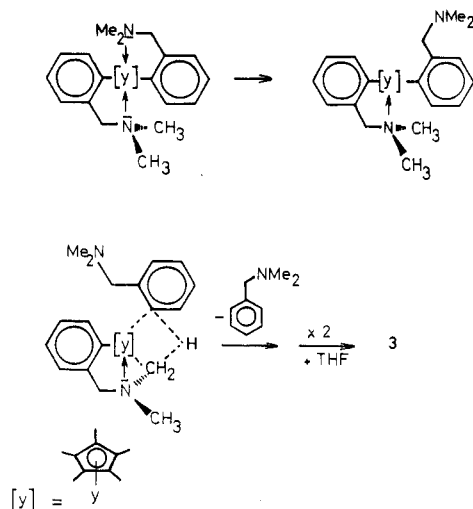


Figure 5. Suggested mechanism for the conversion of 2 to 3.

interaction with the remaining coordinated amine and create space for the usual four-center transition state.<sup>25</sup> Hydrogen is transferred from the N-CH<sub>3</sub> group to the phenyl carbon, and 3 is formed by extrusion of *N,N*-dimethylbenzylamine, dimerization, and uptake of THF.

A mechanism involving oxidative addition of the C-H bond of the N-CH<sub>3</sub> group to the metal center<sup>26</sup> is not possible in d<sup>0</sup> complexes. The C-N bond is not activated although its bond enthalpy is lower than that of the C-H bond.<sup>27</sup> This may be caused by the higher steric crowding and ring strain in the transition state necessary for this reaction.

## Experimental Section

**General Considerations.** All experiments were performed under nitrogen by using standard Schlenk and drybox (Braun MB200) techniques. Solvents were distilled from Na/K alloy and degassed prior to use. IR spectra were recorded on a Pye-Unicam SP3-300 spectrophotometer as Nujol mulls between KBr disks. NMR spectra were recorded on Bruker WH90-DS (<sup>1</sup>H) and Varian VXR-300 (<sup>1</sup>H and <sup>13</sup>C) spectrometers and referenced to solvent resonances, unless specified otherwise. Elemental analyses were determined at the Micro-Analytical Department of the University of Groningen under the supervision of A. F. Hamming. The analyses reported are the average of at least two independent determinations. The synthesis of Y(o-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>3</sub> (1) and Cp\*Y(o-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub> (2) will be described elsewhere.<sup>2c</sup> Cp\*H was synthesized according to published procedures.<sup>28</sup>

Cp\*Y[o-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe(CH<sub>2</sub>-μ)] [μ-o-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe(CH<sub>2</sub>-μ)]Y Cp\*[THF](C<sub>6</sub>H<sub>5</sub>)<sub>1.5</sub> (3). A suspension of 1.06 g (2.2 mmol) of Cp\*Y(o-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub> in 1.0 mL of THF was sealed under vacuum in a glass ampule and heated for 2 weeks at 50 °C during which an orange solution formed. The ampule was opened in a drybox, and the reaction mixture was transferred into a Schlenk vessel. The solvent was removed under vacuum; the orange oil was stripped with two portions of 10 mL of pentane and subsequently extracted with 50 mL of pentane. The pentane was removed under vacuum, and the residue was dissolved in a

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minimal amount of hot benzene. The solution was cooled to 10 °C, and white needles of **3** were formed. The crystals were filtered off, dried under vacuum, and isolated. After concentration of the mother liquor this procedure was repeated twice. Overall yield: 0.41 g (0.45 mmol, 41%) of **3** as the benzene solvate (1.5 mol of benzene/mol of **3**). IR ( $cm^{-1}$ ): 3070 (m), 3060 (s), 3010 (s), 2900 (s), 2810 (s), 2790 (s), 2720 (w), 1955 (w), 1805 (w), 1470 (s), 1440 (s), 1410 (s), 1365 (s), 1355 (m), 1345 (m), 1280 (m), 1260 (w), 1240 (m), 1225 (m), 1160 (m), 1150 (w), 1130 (m), 1085 (m), 1045 (s), 1025 (m), 1010 (s), 995 (s), 985 (m), 975 (m), 915 (w), 865 (m), 825 (w), 810 (w), 800 (m), 740 (s), 710 (w), 680 (s), 625 (w), 585 (w), 535 (s), 515 (m), 475 (m), 450 (s), 430 (m), 415 (s).  $^1H$  NMR (toluene- $d_8$ , 60 °C):  $\delta$  7.50 (m, 1 H, aryl ring CH), 7.17 (s, 4.5 H,  $C_6H_6$ ), 7.10 (m, 2 H, aryl ring CH), 6.90 (m, 1 H, aryl ring CH), 4.10 (d,  $^2J_{HH} = 14.8$  Hz, 1 H, N- $CH_2$ -C(aryl ring)), 3.34 (d,  $^2J_{HH} = 14.8$  Hz, 1 H, N- $CH_2$ -C(aryl ring)), 2.89 (s, br, 2 H,  $\alpha$ -H(THF)), 2.50 (s, 3 H, N- $CH_3$ ), 1.69 (s, 15 H,  $C_5(CH_3)_5$ ), 1.63 (d,  $^2J_{HH} = 15.0$  Hz, 1 H, N- $CH_2$ -Y), 1.30 (s, br, 2 H,  $\beta$ -H(THF)), 1.22 (d,  $^2J_{HH} = 15.0$  Hz, 1 H, N- $CH_2$ -Y).  $^{13}C$  NMR (toluene- $d_8$ , 60 °C):  $\delta$  189.55 (s, br, aryl C-Y), 153.50 (s, aryl C- $CH_2$ ), 145.29 (d,  $^1J_{CH} = 151.9$  Hz, aryl CH), 131.39 (d,  $^1J_{CH} = 156.8$  Hz, aryl CH), 130.31 (d,  $^1J_{CH} = 156.4$  Hz, aryl CH), 129.54 (d,  $^1J_{CH} = 149.1$ , aryl CH), 121.62 (s,  $C_5Me_5$ ), 76.37 (t,  $^1J_{CH} = 132.9$  Hz, C(aryl)- $CH_2$ -N), 75.01 (t,  $^1J_{CH} = 149.0$  Hz,  $\alpha$ -C(THF)), 70.04 (td,  $^1J_{CH} = 117.2$  Hz,  $^1J_{CY} = 28.4$  Hz, N- $CH_2$ -Y), 56.84 (q,  $^1J_{CH} = 134.8$  Hz, N- $CH_3$ ), 30.57 (t,  $^1J_{CH} = 134.2$  Hz,  $\beta$ -C(THF)), 16.56 (q,  $^1J_{CH} = 124.9$  Hz,  $C_5(CH_3)_5$ ).  $^{13}C$  NMR (toluene- $d_8$ , -80 °C):  $\delta$  193.72 (d,  $^1J_{CY} = 46.0$  Hz, aryl C-Y), 175.15 (dd,  $^1J_{CY} = 23.0$  Hz,  $^1J_{CY} = 11.5$  Hz, aryl C-Y), 116.16 (s,  $C_5Me_5$ ), 115.07 (s,  $C_5Me_5$ ), 72.18 (t,  $^1J_{CH} = 133.5$  Hz, C(aryl)- $CH_2$ -N), 69.54 (t,  $^1J_{CH} = 148.5$  Hz,  $\alpha$ -C(THF)), 68.71 (t,  $^1J_{CH} = 133.5$  Hz, C(aryl)- $CH_2$ -N), 65.30 (td,  $^1J_{CH} = 116.9$  Hz,  $^1J_{CY} = 34.5$  Hz, N- $CH_2$ -Y), 60.80 (td,  $^1J_{CH} = 116.9$  Hz,  $^1J_{CY} = 19.6$  Hz, N- $CH_2$ -Y), 52.02 (q,  $^1J_{CH} = 135.8$  Hz, N- $CH_3$ ), 50.06 (q,  $^1J_{CH} = 137.0$  Hz, N- $CH_3$ ), 25.48 (t,  $^1J_{CH} = 133.5$  Hz,  $\beta$ -C(THF)), 11.96 (q,  $^1J_{CH} = 124.3$  Hz,  $C_5(CH_3)_5$ ), 11.29 (q,  $^1J_{CH} = 124.3$  Hz,  $C_5(CH_3)_5$ ). The remaining signals of the aryl rings overlap with solvent resonances and were not assigned. Anal. Calcd for  $C_{42}H_{60}N_2OY_2 \cdot (C_6H_6)_{1.5}$ : C, 67.77; H, 7.69; N, 3.10; Y, 19.67. Found: C, 68.05; H, 7.90; N, 2.88; Y, 19.40.

**Structure Determination of 2.** A colorless crystal of **2**, obtained by slowly cooling a saturated pentane solution to -30 °C, was cut from a large needle in its longest dimension, glued on the top of a glass fiber, and directly transferred into the cold nitrogen stream of the low-temperature unit mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a PDP-11/23 computer. Crystal data and other details of the structure determination are collected in Table IV. Unit cell parameters and their standard deviations were determined from a least-squares treatment of the setting angles of 24 reflections in the range  $7.01^\circ < \theta < 18.66^\circ$ . The monoclinic unit cell was checked for the presence of higher lattice symmetry.<sup>29</sup> Crystal and instrumental instability were monitored through the measurement of three reference reflections that were collected after every 170 min of the X-ray exposure time. A  $360^\circ \Psi$  scan for a close to axial reflection showed a variation in the intensity up to 11% about the mean value. The net intensities of the data were corrected for the scale variation, for Lorentz and polarization effects, and for absorption.<sup>30</sup> Variance  $\sigma^2(I)$  was calculated on the basis of counting statistics and a term  $P^2I^2$  where  $P$  ( $= 0.13$ ) is the instability constant as derived from the excess variance in the reference reflections.<sup>31</sup> The structure was solved by direct methods<sup>32</sup> and refined on  $F$  by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and isotropic temperature factors for hydrogen. Most of the hydrogen atoms were located on subsequent Fourier difference maps. The remaining were initially placed at calculated positions and subsequently refined satisfactorily. Isotropic sec-

Table IV. Details on the Structure Determinations of **2** and **3**

	2	3
a. Crystal Data		
chemical formula	$C_{42}H_{60}N_2Y$	$C_{42}H_{60}N_2OY_2 \cdot (C_6H_6)_{1.5}$
mol wt	492.52	903.93
cryst system	monoclinic	monoclinic
space group, No.	$P2_1/n$ , 14	$P2_1/c$ , 14
$a$ , Å	18.607 (4)	17.004 (1)
$b$ , Å	15.633 (3)	13.962 (1)
$c$ , Å	8.861 (3)	20.129 (3)
$\beta$ , deg	102.73 (3)	92.94 (1)
$V$ , Å <sup>3</sup>	2514 (1)	4772.3 (8)
$Z$	4	4
$D_{calc}$ , g·cm <sup>-3</sup>	1.301	1.258
$F(000)$ , electrons	1040	1900
$\mu$ , cm <sup>-1</sup>	23.5 (Mo $K\alpha$ )	35.6 (Cu $K\alpha$ )
approx cryst dimens, mm	$0.10 \times 0.15 \times 0.15$	$0.85 \times 0.35 \times 0.23$
b. Data Collection		
radiatn, Å	Mo $K\alpha$ , 0.71073	Cu $K\alpha$ , 1.54178
monochromator	graphite	Ni filter
temp, K	130	294
$\theta$ range (min, max), deg	1.13, 27.0	2.2, 70.0
$\omega/2\theta$ scan, deg	$\Delta\omega = 0.90 + 0.35 \tan \theta$	$\Delta\omega = 0.50 + 0.15 \tan \theta$
data set		
$h$	-23→23	-20→20
$k$	0→19	0→17
$l$	0→11	-24→0
cryst to receiving aperture dist, mm	173	173
horizontal, vertical aperture, mm	$3.2 + \tan \theta$ , 4.5	3.0, 6.0
reference reflns, rms dev in %	$\bar{2}42$ , 4.5; 572, 4.5; 731, 5.0	$10\bar{2}$ , 0.6; $12\bar{2}$ , 0.6; $31\bar{1}$ , 0.6
drift correctn	1.00-1.19	1.00-1.034
min and max empirical absorpntn corr fac	0.87-1.19	0.91-1.47
X-ray exposure time, h	234.3	174.7
total data	5999	9851
unique data	5426	9015
obsd data	3007 ( $F > 4.0\sigma(F)$ )	4578 ( $F > 5.0\sigma(F)$ )
c. Refinement		
no. of reflns	3006	4578
no. of refined parameters	438	532
final $R_F = \sum( F_o  -  F_c ) / \sum F_o $	0.053	0.065
final $wR = [\sum(w( F_o  -  F_c )^2) / \sum wF_o^2]^{1/2}$	0.068	0.070
weighting scheme	$1/\sigma^2(F)$	$1/[\sigma^2(F) + 0.000853F^2]$
$S = (\sum w( F_o  -  F_c )^2 / (m - n))^{1/2}$	0.923	3.52
residual electron density in final diff Fourier map, e/Å <sup>3</sup>	-0.88, 1.07	-0.64, 0.52
max (shift/ $\sigma$ ) final cycle	0.845	0.111
average (shift/ $\sigma$ ) final cycle	0.0919	0.009

<sup>a</sup>  $m$  = number of observations.  $n$  = number of variables.

ondary extinction was applied.<sup>33</sup> Reflection 5,10, $\bar{8}$  suffered from a measurement mismatch and was left out of the refinement. The final values of the refinement positional parameters for the non-hydrogen atoms are given in Table V. Neutral atom scattering factors<sup>34</sup> were used with anomalous dispersion corrections<sup>35</sup> being applied to the non-hydrogen atoms. All calculations were carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program XTAL,<sup>36</sup> the EUCLID<sup>37</sup> package,

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Table V. Final Fractional Coordinates and Equivalent Isotropic Thermal Parameters for Non-Hydrogen Atoms of 2 and 3

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{eq}, \text{\AA}^2$	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{eq}, \text{\AA}^2$
2									
Y(1)	0.00747 (3)	0.22939 (3)	0.24086 (6)	0.0155 (2)	C(14)	0.2076 (4)	0.1455 (5)	-0.003 (1)	0.054 (3)
N(1)	-0.0830 (3)	0.1591 (3)	0.0139 (5)	0.023 (2)	C(15)	0.1397 (4)	0.1761 (4)	0.0161 (8)	0.038 (3)
N(2)	0.0847 (3)	0.1405 (4)	0.4508 (7)	0.039 (2)	C(16)	0.1623 (4)	0.1452 (6)	0.441 (1)	0.056 (3)
C(1)	-0.0964 (3)	0.1645 (4)	0.3339 (7)	0.025 (2)	C(17)	0.0697 (4)	0.1474 (5)	0.6031 (7)	0.041 (2)
C(2)	-0.1336 (3)	0.1020 (4)	0.2304 (6)	0.020 (2)	C(18)	0.0612 (6)	0.0485 (5)	0.3945 (9)	0.065 (4)
C(3)	-0.1990 (3)	0.0628 (4)	0.2482 (7)	0.026 (2)	C(19)	0.0685 (3)	0.3771 (4)	0.3556 (7)	0.029 (2)
C(4)	-0.2297 (4)	0.0853 (4)	0.3716 (8)	0.035 (2)	C(20)	0.0645 (3)	0.3803 (4)	0.1932 (7)	0.027 (2)
C(5)	-0.1960 (4)	0.1472 (4)	0.4761 (7)	0.032 (2)	C(21)	-0.0105 (3)	0.3836 (4)	0.1154 (7)	0.025 (2)
C(6)	-0.1306 (3)	0.1848 (4)	0.4560 (7)	0.024 (2)	C(22)	-0.0533 (3)	0.3826 (4)	0.2311 (7)	0.021 (2)
C(7)	-0.1028 (3)	0.0803 (4)	0.0918 (7)	0.024 (2)	C(23)	-0.0048 (4)	0.3787 (4)	0.3763 (7)	0.025 (2)
C(8)	-0.0493 (4)	0.1336 (4)	-0.1147 (7)	0.032 (2)	C(24)	0.1379 (4)	0.3849 (6)	0.480 (1)	0.056 (3)
C(9)	-0.1513 (3)	0.2055 (4)	-0.0502 (7)	0.028 (2)	C(25)	0.1303 (4)	0.3903 (4)	0.1196 (9)	0.045 (3)
C(10)	0.1154 (3)	0.1708 (4)	0.1558 (7)	0.026 (2)	C(26)	-0.0372 (4)	0.3913 (5)	-0.0555 (7)	0.037 (2)
C(11)	0.1667 (5)	0.1363 (6)	0.2709 (9)	0.071 (4)	C(27)	-0.1358 (4)	0.3917 (4)	0.2051 (8)	0.035 (2)
C(12)	0.2351 (6)	0.1021 (9)	0.256 (1)	0.118 (5)	C(28)	-0.0238 (4)	0.3849 (4)	0.5336 (8)	0.034 (2)
C(13)	0.2534 (4)	0.1077 (7)	0.113 (1)	0.084 (4)					
3									
Y(1)	0.25211 (4)	0.16888 (6)	0.14025 (4)	0.0423 (3)	C(20)	0.1331 (8)	0.507 (1)	0.3034 (8)	0.121 (8)
Y(2)	0.32528 (4)	0.38459 (6)	0.16660 (4)	0.0423 (3)	C(21)	0.109 (1)	0.556 (1)	0.2466 (7)	0.21 (1)
O(1)	0.2153 (3)	0.4642 (4)	0.2176 (3)	0.063 (2)	C(22)	0.1564 (7)	0.528 (1)	0.1909 (6)	0.121 (7)
N(1)	0.2674 (4)	0.4042 (5)	0.0560 (3)	0.051 (3)	C(23)	0.4750 (5)	0.4153 (7)	0.2116 (5)	0.051 (3)
N(2)	0.2998 (4)	0.1414 (5)	0.2532 (3)	0.048 (3)	C(24)	0.4311 (6)	0.4578 (8)	0.2591 (5)	0.059 (4)
C(1)	0.3807 (5)	0.2545 (6)	0.0936 (4)	0.049 (3)	C(25)	0.3915 (6)	0.5380 (8)	0.2287 (6)	0.066 (4)
C(2)	0.3756 (5)	0.2883 (7)	0.0273 (5)	0.052 (3)	C(26)	0.4135 (6)	0.5427 (7)	0.1627 (6)	0.064 (4)
C(3)	0.4282 (5)	0.2598 (7)	-0.0198 (5)	0.065 (4)	C(27)	0.4660 (6)	0.4662 (8)	0.1520 (5)	0.061 (4)
C(4)	0.4868 (6)	0.1951 (8)	-0.0028 (6)	0.076 (5)	C(28)	0.5315 (6)	0.3351 (7)	0.2240 (6)	0.084 (5)
C(5)	0.4931 (6)	0.1577 (7)	0.0598 (5)	0.070 (4)	C(29)	0.4306 (6)	0.4312 (8)	0.3317 (5)	0.090 (5)
C(6)	0.4419 (5)	0.1884 (7)	0.1064 (5)	0.058 (3)	C(30)	0.3469 (7)	0.6111 (8)	0.2675 (7)	0.114 (6)
C(7)	0.3157 (5)	0.3612 (7)	0.0047 (5)	0.063 (4)	C(31)	0.3922 (7)	0.6209 (9)	0.1136 (6)	0.118 (7)
C(8)	0.2233 (6)	0.4856 (7)	0.0259 (5)	0.073 (4)	C(32)	0.5106 (6)	0.4501 (8)	0.0893 (5)	0.088 (5)
C(9)	0.2156 (5)	0.3318 (7)	0.0853 (5)	0.055 (4)	C(33)	0.1626 (8)	0.0737 (8)	0.0465 (7)	0.079 (5)
C(10)	0.1460 (5)	0.2065 (6)	0.2132 (4)	0.049 (3)	C(34)	0.1476 (7)	0.029 (1)	0.1043 (8)	0.081 (6)
C(11)	0.1620 (5)	0.1822 (7)	0.2798 (5)	0.056 (3)	C(35)	0.213 (1)	-0.0172 (9)	0.1278 (7)	0.098 (7)
C(12)	0.1118 (6)	0.2048 (8)	0.3294 (5)	0.076 (5)	C(36)	0.2712 (7)	-0.002 (1)	0.086 (1)	0.093 (7)
C(13)	0.0413 (7)	0.2524 (8)	0.3137 (6)	0.082 (5)	C(37)	0.241 (1)	0.055 (1)	0.0341 (6)	0.092 (6)
C(14)	0.0216 (6)	0.2764 (8)	0.2477 (6)	0.079 (5)	C(38)	0.105 (1)	0.126 (1)	0.0016 (8)	0.24 (1)
C(15)	0.0747 (5)	0.2536 (7)	0.1997 (5)	0.068 (4)	C(39)	0.0709 (8)	0.016 (1)	0.1340 (9)	0.24 (1)
C(16)	0.2357 (5)	0.1296 (7)	0.2997 (5)	0.063 (4)	C(40)	0.220 (1)	-0.087 (1)	0.1877 (7)	0.25 (1)
C(17)	0.3676 (6)	0.0821 (7)	0.2751 (5)	0.072 (4)	C(41)	0.3537 (8)	-0.047 (1)	0.091 (1)	0.29 (2)
C(18)	0.3228 (6)	0.2447 (7)	0.2465 (5)	0.050 (3)	C(42)	0.283 (1)	0.076 (1)	-0.0267 (7)	0.34 (2)
C(19)	0.1967 (6)	0.4377 (8)	0.2846 (5)	0.077 (5)					

$${}^a U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

and a locally extended version of the program PLUTO.<sup>38</sup>

**Structure Determination of 3.** A colorless, needle shaped crystal of 3, obtained by slowly cooling a saturated benzene solution of 3 (vide supra), was sealed in a 0.5-mm Lindemann capillary and transferred to an Enraf-Nonius CAD-4F diffractometer for data collection at room temperature (Table IV). Unit cell parameters were determined from a least-squares treatment of the setting angles of 25 reflections in the range  $9.9^\circ < \theta < 18.5^\circ$ . Unit-cell parameters were checked for the presence of higher lattice symmetry.<sup>29</sup> Data were corrected for  $Lp$ , for a small linear decay, and for absorption.<sup>30</sup> Standard deviations as obtained by counting statistics were increased according to an analysis of the excess variance of the three reference reflections:  $\sigma^2(I) = \sigma_{cs}^2(I) + (0.011I)^2$ .<sup>31</sup> Space group  $P2_1/c$  was determined from the systematic extinctions  $h0l$  ( $l = 2n + 1$ ) and  $0k0$  ( $k = 2n + 1$ ). The yttrium atoms were located with standard Patterson methods,<sup>32</sup> and the remaining non-hydrogen atoms were located from subsequent difference Fourier maps. The hydrogen atoms of C(9) and C(18) were also located from a difference map; the other hydrogen atoms were introduced at calculated positions. Re-

finement on  $F$  was carried out by blocked full-matrix least-squares techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters; the benzene solvate molecules were included in the refinement with bond restraints and constraints. Hydrogen atoms on C(9) and C(18) were refined with a common isotropic thermal parameter; other hydrogen atoms were refined riding on their carrier atom with separate common isotropic thermal parameters for the complex molecule and the benzene molecules. Weights were introduced in the final refinement cycles; convergence was reached at  $R = 0.065$ . The Cp\* ring C(33)–C(37) shows relatively high rotational thermal motion. The THF ligand is probably disordered for C(21) as is indicated by its thermal motion ellipsoid having the largest component perpendicular to the ring plane. Final atomic coordinates and equivalent thermal parameters of the complex are listed in Table V, selected data on the geometry are given in Table II. Crystal data and numerical details of the structure determination are given in Table IV. Neutral atom scattering factors were taken from Cromer and Mann<sup>34</sup> and corrected for anomalous dispersion.<sup>35</sup> All calculations were performed with SHELX76<sup>40</sup> and the EUCLID package<sup>37</sup> (geometrical calculations and illustrations on a MicroVAX-II computer).

**Acknowledgment.** This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organi-

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zation for Scientific Research (NWO). We thank Dr. S. Gambarotta for his valuable advice concerning the single-crystal sampling, A. J. M. Duisenberg for the data collection of **3**, and H. van der Heijden, Dr. E. J. M. de Boer, and Dr. C. J. Schaverien (Shell Research BV) for stimulating discussions.

Registry No. 2, 122470-83-1; 3, 122487-83-6.

Supplementary Material Available: ORTEP<sup>99</sup> drawings of **2** and **3** and tables of all atomic coordinates, thermal parameters, bond distances, bond angles, and torsion angles (28 pages); listings of observed and calculated structure factors (78 pages). Ordering information is given on any current masthead page.

## Reactivity Studies of the Zirconium-Induced Insertion of Isonitriles into a 1-Sila-3-zirconacyclobutane Ring. Structural and Chemical Evidence of "Carbenium-Like" Intermediates for the Intramolecular 1,2-Silyl Shift and Reductive Coupling Reactions

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Received May 15, 1989

The reaction of CNMe with  $\text{Cp}^*_2\text{Zr}(\text{CH}_2\text{SiMe}_2\text{CH}_2)$  follows two different competitive pathways depending on the reaction conditions. At 25 °C, the lateral insertion of each equivalent of CNMe is accompanied by a 1,2-silyl shift and the stepwise formation of  $\text{Cp}^*_2\text{Zr}(\text{N}(\text{Me})\text{C}(\text{=CH}_2)\text{SiMe}_2\text{CH}_2)$  (**1**) and  $\text{Cp}^*_2\text{Zr}(\text{N}(\text{Me})\text{C}(\text{=CH}_2)\text{SiMe}_2(\text{CH}_2\text{=})\text{CN}(\text{Me}))$  (**2**). Alternatively, upon repeating the reaction at -20 °C in the presence of excess CNMe, reductive coupling of two molecules of CNMe occurs with the formation of  $\text{Cp}^*_2\text{Zr}(\text{N}(\text{Me})\text{C}(\text{CH}_2\text{SiMe}_2\text{CH}_2)\text{=CN}(\text{Me}))$  (**3**). Structural and chemical evidence regarding the nature of the reactive intermediates involved in these intramolecular processes has been provided by an investigation of the reaction of *tert*-butyl isocyanide with  $\text{Cp}_2\text{Zr}(\text{CH}_2\text{SiMe}_2\text{CH}_2)$  at 25 °C. Nucleophilic attack by the first equivalent of CN-*t*-Bu is accompanied by lateral insertion into a Zr-C bond and the formation of  $\text{Cp}_2\text{Zr}(\text{N}(\text{CMe}_3)\text{CCH}_2\text{SiMe}_2\text{CH}_2)$  (**6**). The reaction of this  $\eta^2$ -iminoacyl species with a second equivalent of CN-*t*-Bu proceeds with reductive coupling of two molecules of CN-*t*-Bu and the formation of  $\text{Cp}_2\text{Zr}(\text{N}(\text{CMe}_3)\text{C}-\text{C}(\text{=NCMe}_3)\text{CH}_2\text{SiMe}_2\text{CH}_2)$  (**7**) which upon thermolysis cleanly rearranges in solution to  $\text{Cp}_2\text{Zr}(\text{N}(\text{CMe}_3)\text{C}(\text{CH}_2\text{SiMe}_2\text{CH}_2)\text{=CN}(\text{CMe}_3))$  (**8**). The molecular structures of **6** and **7** have been verified by X-ray diffraction methods. Crystal data for **6** at 25 °C: monoclinic space group  $P2_1/n$  with  $a = 14.034$  (3) Å,  $b = 15.550$  (4) Å,  $c = 9.336$  (2) Å,  $\beta = 93.14$  (2)°,  $Z = 4$ . For **7** at 25 °C: monoclinic space group  $P2_1/c$  with  $a = 8.422$  (3) Å,  $b = 18.552$  (5) Å,  $c = 16.318$  (6) Å,  $\beta = 102.63$  (3)°,  $Z = 4$ . The resulting structural information provides valuable insight into the nature of the "carbenium-like" intermediates involved in the intramolecular 1,2-silyl shift and reductive coupling reactions observed for 1-sila-3-zirconacyclobutane and related electrophilic complexes.

### Introduction

Electron-deficient metal alkyl derivatives readily induce the migratory insertion of carbon monoxide into a metal-carbon bond.<sup>1-14</sup> The reactivity exhibited by the cor-

responding  $\eta^2$ -acyl complexes was initially attributed to an "oxycarbene" representation of the electronic structure

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