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Synthesis of Monomeric Permethylyttrocene Derivatives. The Crystal Structures of Cp*$_2$YN(SiMe$_3$)$_2$ and Cp*$_2$YCH(SiMe$_3$)$_2$[1,3]

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The reactions of Cp*$_2$YCl·THF (2) with NaN(SiMe$_3$)$_2$ and LiCH(SiMe$_3$)$_2$ yield the monomeric complexes Cp*$_2$YN(SiMe$_3$)$_2$ (3) and Cp*$_2$YCH(SiMe$_3$)$_2$ (4), respectively. The crystal structures of 3 and 4 were determined by X-ray diffraction methods. The crystals of 3 are monoclinic, space group $P2_1/c$, with a = 11.466 (2) Å, b = 15.684 (8) Å, c = 31.557 (9) Å, β = 96.36 (2)°, and Z = 8. The structure was refined to R = 0.044. The molecular structures of this complex feature remarkably short Y–N distances (2.274 (5) and 2.253 (5) Å) and Y–methyl contacts. Crystals of 4 are monoclinic, space group $I2/c$, with a = 17.998 (8) Å, b = 21.758 (8) Å, c = 14.591 (4) Å, β = 92.39 (3)°, and Z = 8. The structure was refined to R = 0.073. The molecular structure exhibits besides a short Y-methyl contact an "α-agostic Y···CH interaction". The yttrium–methyl interactions were also studied by solid-state CP ^{13}C NMR. At room temperature 3 shows two and 4 shows three separate resonances of methyl groups bonded to silicon, supporting the conclusion that in 4 the methyl–yttrium interaction is stronger than in 3. A convenient synthesis of Cp*Na (1) is described.

Introduction

The rapid growth of organolanthanoid chemistry during the last years has produced many exciting results.[4] In particular the work by Watson on Cp*$_2$LuR compounds[5] drew our attention to analogues of group 3 (Sc, Y, La) and other early transition metals. A recent publication on permethylscandocene derivatives[6] illustrates the very interesting and unexpected chemistry of this class of compounds. Our group has reported extensively on the chemistry of Cp$_2$TiR compounds[7] and is currently working on the permethyl analogues.[7] The work mentioned above stimulated our interest in group 3 organometallics and especially in monomeric, coordinatively unsaturated, permethylyttrocene complexes, which are expected to show unique chemical behavior. Therefore we started a study to explore this field, and the results are presented in this paper.

Experimental Section

General Remarks. All compounds are extremely air-sensitive. Manipulations were carried out under nitrogen using glovebox (Braun MB-200) and Schlenkline techniques.

Physical Measurements. IR spectra (Nujol/KBr) were obtained by using a Pye Unicam SP3-300 spectrophotometer. Solution NMR spectra were recorded on Nicolet NT200, Bruker-WH-90, and Hitachi-Perkin Elmer R-24B spectrometers. The solid-state ^{13}C NMR spectra were measured on a Bruker-CXP-200 operating at 25 °C, applying cross-polarization (CP) and magic-angle-spinning (MAS) techniques; the cross-polarization time used was 2 ms. Elemental analyses were carried out at the Micro Analytical Group of the Chemical Laboratories of this university under supervision of Mr. A. F. Hamminga.

Materials. Solvents (pentane, Et$_2$O, THF, toluene) were predried over Na wire and distilled from Na/K alloy benzophenone ketyl prior to use. Cp*H was synthesized by Burgers method.[8] YCl$_3$·3THF was made by continuous extraction of YCl$_3$ with THF; YCl$_3$ was obtained by dissolving Y$_2$O$_3$ (Aldrich) in hydrochloric acid and dehydrating with SOCl$_2$.[9] NaN(SiMe$_3$)$_2$[10] and LiCH(SiMe$_3$)$_2$[11] were prepared according to published procedures.

New Preparations. Detailed syntheses of the new compounds, their elemental analyses, and IR and ^{1}H NMR spectra are reported here. The ^{13}C NMR data are given in Table I.

Cp*Na (1). A mixture of NaH (Fluka, washed with pentane) (0.81 g, 33.8 mmol) in 50 mL of THF and Cp*H (4.80 g, 35.2 mmol) was refluxed for 6 h. After the mixture was cooled, the solids were filtered off to give a clear light brown solution which was concentrated to 25 mL. After crystallization at −30 °C, the mother liquor was decanted and the product washed with pentane: yield 3.17 g of 1 (20.0 mmol, 57% based on Cp*H); IR (cm^{-1}) 2720 (w), 1365 (m), 1268 (w), 1160 (w), 1080 (m), 1060 (w), 1000 (w), 810 (m), 723 (m), 645 (m), 470 (w), 400 (m), 330 (m); ^{1}H NMR (THF-d_8, 25 °C) δ 1.88 (s). Anal. Calcd for C$_{10}$H$_{15}$Na: C, 75.91; H, 9.56; Na, 14.57. Found: C, 75.12; H, 9.41; Na, 14.53.

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[1] This work was presented in part at the NATO-ASI on "Fundamental and Technological Aspects of Organo-f-Element Chemistry" held in Acquafredda di Maratea, Italy, Sept 10–21, 1984, and preliminary results were published in: Den Haan, K. H.; Teuben, J. H. *Recl. Trav. Chim. Pays-Bas* **1984**, *103*, 333–334.

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[3] In this paper the following abbreviations are used: Cp = η^5-C$_5$H$_5$; Cp′ = η^5-C$_5$H$_4$Me; Cp* = η^5-C$_5$Me$_5$.

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Table I. ^{13}C NMR Spectra

complex	assign.	solution^a δ	solution^a $^1J_{\mathrm{C-H}}$, Hz	solid state δ	solid state int
2	$C_5\mathrm{Me}_5$	118.10		*b*	*b*
	C_5Me_5	11.70	125.0	*b*	*b*
	α-THF	71.97	147.6	*b*	*b*
	β-THF	25.37	133.9	*b*	*b*
3	$C_5\mathrm{Me}_5$	119.71		120.3	10
				119.7	
	C_5Me_5	12.15	125.7	13.8	10
	SiMe_3	5.24	116.0	13.1	3
				6.6	3
4	$C_5\mathrm{Me}_5$	119.14		120.5	4
		119.75		119.9	4
				119.0	2
	C_5Me_5	11.78	125.5	13.5	10
		12.10	125.6		
	$\mathrm{Si}Me_3$	5.02	116.6	13.5	1
				7.8	3
				4.2	2
	$\mathrm{Y}C\mathrm{HSi}_2$	25.19	84.2 ($J_{\mathrm{Y-C}}$ = 36.6)	25.6 ($J_{\mathrm{Y-C}}$ = 41 ± 4 Hz)	1

^{a} δ relative to $\mathrm{Me_4Si}$ (δ 0); all spectra in $\mathrm{C_6D_6}$ at 25 °C. ^{b} Not measured.

This preparation can be scaled up (0.25 mol) conveniently. The reflux time must be adjusted till hydrogen evolution has stopped (approximately 2 days). The crystallization step can be omitted. Instead, after filtration the solvent THF was removed under vacuum as far as possible, and the crude material was washed with pentane to give high yields (>90%) of 1. The purity was normally better than 98% (elemental analysis and ^{1}H NMR).

$\mathbf{Cp^*_2YCl{\cdot}THF}$ (2). A solution of 1 in THF (50.3 mL, 0.38 M) was added to a suspension of 8.5 g of $\mathrm{YCl_3{\cdot}3THF}$ (19.1 mmol) in 300 mL of THF at 0 °C. The mixture was refluxed for 3 h. After the solution was cooled, the solvent was completely removed by evaporation. The remaining solids were extracted with 100 mL of toluene, and the clear solution was concentrated to 50 mL. After crystallization at −30 °C, the mother liquor was removed and the crystals were washed with pentane. After the crystals were dried in vacuo, 5.55 g (11.9 mmol, 62%) of 2 was isolated as white crystals: IR (cm^{-1}) 2720 (w), 1490 (m), 1365 (m), 1342 (s), 1035 (s), 1015 (s), 915 (m), 860 (s), 839 (m), 800 (w), 737 (m), 673 (m), 595 (w), 375 (m); ^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C) δ 1.19 (m, 4 H, β-THF), 2.01 (s, 30 H, $\mathrm{C_5Me_5}$), 3.42 (m, 4 H, α-THF). Anal. Calcd for $\mathrm{C_{24}H_{38}YClO}$: C, 61.74; H, 8.20; Y, 19.04; Cl, 7.59; M_r (cryoscopic, $\mathrm{C_6H_6}$), 467. Found: C, 61.49; H, 8.20; Y, 18.90; Cl, 7.64; M_r, 463 ± 7.

$\mathbf{Cp^*_2YN(SiMe_3)_2}$ (3). To a solution of 0.62 g of 2 (1.33 mmol) in 25 mL of toluene was added 6.3 mL of a toluene solution of $\mathrm{NaN(SiMe_3)_2}$ (0.21 M). While the solution was stirred at room temperature, a white suspension formed. After 6 h, the toluene was pumped off and the solids were extracted with pentane. The combined extracts were concentrated to 30 mL. When the mixture was cooled to −30 °C, large colorless crystals formed: yield 0.42 g (0.81 mmol, 61%) of 3; IR (cm^{-1}) 2720 (w), 1490 (m), 1365 (m), 1253 (s), 1245 (s), 1180 (w), 1000 (s), 869 (s), 835 (m), 820 (s), 774 (m), 748 (m), 665 (m), 600 (m), 380 (m); ^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C) δ 0.14 (s, 18 H, $\mathrm{SiMe_3}$), 1.93 (s, 30 H, $\mathrm{C_5Me_5}$). Anal. Calcd for $\mathrm{C_{26}H_{48}YSi_2N}$: C, 60.08; H, 9.23; Y, 17.11; M_r (cryoscopic, $\mathrm{C_6H_6}$), 520. Found: C, 59.35; H, 9.31; Y, 16.59; M_r, 507 ± 7.

$\mathbf{Cp^*_2YCH(SiMe_3)_2}$ (4). A solution of $\mathrm{LiCH(SiMe_3)_2}$ in $\mathrm{Et_2O}$ (22 mL, 0,25 M) was added with stirring to a suspension of 2.55 g of 2 (5.46 mmol) in 75 mL of $\mathrm{Et_2O}$ at 0 °C. After being warmed to room temperature, the reaction mixture was stirred for 2 h. The $\mathrm{Et_2O}$ was removed under vacuum, and the solids were extracted with pentane. The clear pentane solution was concentrated until crystallization started and then stored overnight at −30 °C. The large colorless crystals were filtered off to give 1.34 g of 4. Concentration of the mother liquor gave a second crop: overall yield, 1.94 g (3.76 mmol, 69%) of 4; IR (cm^{-1}) 2720 (w), 1365 (m), 1250 (s), 1239 (s), 1035 (s, br), 835 (s, br), 760 (m), 720 (w), 965 (w), 650 (m), 590 (m), 385 (m); ^{1}H NMR ($\mathrm{C_6D_6}$, 25 °C) δ −0,10 (d, 1 H, Y–CH, $^2J_{\mathrm{Y-H}}$ = 2.3 Hz), 0,17 (s, 18 H, $\mathrm{SiMe_3}$), 1.87 (s, 15 H, $\mathrm{C_5Me_5}$), 1.93 (s, 15 H, $\mathrm{C_5Me_5}$). Anal. Calcd for $\mathrm{C_{27}H_{49}YSi_2}$: C, 62.51; H, 9.54; Y, 17.14; M_r (crysocopic, $\mathrm{C_6H_6}$), 519. Found: C, 62.53; H, 9.52; Y, 17.06; M_r, 502 ± 7.

Structure Determination and Refinement of 3 and 4. Crystal data and other details of the structure determination are collected in Table II. Crystals of 4 were obtained by recrystallization from diethyl ether. A preliminary structure determination on crystals that were crystallized from pentane showed its structure to be disordered for the Cp* rings and isomorphous with the corresponding Nd analogue.[12]

The colorless transparent crystals of 3 and 4 for the structure determination were selected in a glovebox, mounted on a glass fiber, and transferred immediately into the cold nitrogen stream of the low-temperature unit of an Enraf-Nonius CAD4F diffractometer.

Unit cell parameters were determined from a least-squares of the setting of 14 reflections in the range $20 < \theta < 21°$ for 3 and 20 reflections in the range $20 < \theta < 22°$ for 4. The data were corrected for the decay, Lorentz, and polarization effects. Absorption corrections were not applied since ψ scans for close to axial reflection showed only a small intensity variation.

The Y atoms were obtained by direct methods (MULTAN 80[13]) and Patterson techniques, respectively. The other non-hydrogen atoms were located by standard Fourier techniques. Hydrogen atoms for 3 were located from difference Fourier syntheses. However, since refinement did not improve the geometry of a few methyl groups [C(6), C(8), C(20), C(22), and C(44)], their H atoms were introduced at calculated positions (C–H = 1.08 Å) and refined with fixed geometry with respect to their carrier atoms. For 4, hydrogen atoms were introduced on calculated positions and refined as in 3 except for those on C(1) and C(2) where the positional parameters where refined as well. The structures were refined with least-squares techniques on F with anisotropic thermal temperature factors for the non-hydrogen atoms. The final coordinates of the non-hydrogen atoms are given in Tables III and IV. Scattering factors were taken from ref 14 and anomalous dispersion corrections from ref 15.

The data collection was done with a modified CAD4F software package.[16] The calculations were carried out on an in-house DG-ECLIPSE S/230 minicomputer using a locally modified SHELX76[17] implementation, on the CDC-CYBER/855 of the

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Table II. Crystal Data and Details of the Structure Analysis for $Cp^*_2YN(SiMe_3)_2$ (3) and $Cp^*_2YCH(SiMe_3)_2$ (4)

	3	4
(a) Crystal Data		
empirical formula	$C_{26}H_{48}NSi_2Y$	$C_{27}H_{49}Si_2Y$
mol wt	519.76	518.77
crystallized from	pentane	diethyl ether
cryst system	monoclinic	monoclinic
space group	No. 14, $P2_1/c$	No. 15, $I2/c$
a, Å	11.466 (2)	17.998 (8)
b, Å	15.684 (8)	21.758 (8)
c, Å	31.557 (9)	14.591 (4)
β, deg	96.36 (2)	92.39 (3)
V, Å^3	5640 (3)	5709 (4)
Z	8	8
D(calcd), g/cm^3	1.224	1.207
F(000), electrons	2224	2224
μ(Mo Kα), cm^{-1}	21.8	21.5
cryst size, mm	0.2 × 0.2 × 0.3	0.17 × 0.25 × 0.40
(b) Data Collection		
temp, K	98	108
radiatn, Å	Mo Kα, 0.71073	Mo Kα, 0.71073
θ_{min}, θ_{max}, deg	0.1, 20.5	0.1, 28.5
$\omega/2\theta$ scan, deg	$0.5 + 0.35 \tan\theta$	$0.9 + 0.35 \tan\theta$
hor and vert apert, mm	1.30, 6.00	4.2, 4.5
cryst to detector, mm	173	173
std reflctns	−6,0,0; 0,−6,0; 0,0,8	7,2,1; 1,6,−3; 0,3,5
decay, %	3	1
X-ray exposure time, h	30	84
total data	6063	14426
total unique	5149	7229
obsd data ($I > 2.5\sigma(I)$)	3716	4078
(c) Refinement		
no. of reflctns	3711	4078
no. of parameters	786	329
R	0.044	0.073
wR	0.061	0.057
w^{-1}	$\sigma^2(F)$	$\sigma^2(F)$
$(\Delta/\sigma)_{av}$	0.07	0.07
min and max dens, e Å^{-3}	−0.71, 0.61	−1.1, 1.1

University of Utrecht with programs of the EUCLID package[18] (calculation of geometrical data and preparation of illustrations including an extended version of PLUTO).

Results and Discussion

I. Synthesis. The synthetic strategy we selected to synthesize monomeric Cp^*_2YR complexes was based on $Cp^*_2YCl\cdot THF$ (2) as the starting compound. The latter is easily available from 1 and $YCl_3\cdot 3THF$ (eq 1). The

$$\underset{1}{2Cp^*Na} + YCl_3\cdot 3THF \xrightarrow[\text{reflux}]{\text{THF}} \underset{2}{Cp^*_2YCl\cdot THF} + 2NaCl \qquad (1)$$

reaction of 2 with small carbyl group (R) introducing lithium or Grignard reagents (RM, M = Li, MgX; R = Me, Ph, etc.) is complicated by the incorporation of the salt formed during this reaction[19] to give complexes of the type $Cp^*_2YR\cdot MCl\cdot L$. These complexes are similar to those reported by Watson for ytterbium and lutetium.[20] This complexed salt problem has not yet been encountered sofar in the permethylscandocene[6] and permethyltitanocene[7] chemistry. We suppose that in addition to the high Lewis acidity the large size of an yttrium atom is the reason for this undesired salt complexation. It was assumed that with bulky ligands the complexed salt problem might be circumvented.

It was indeed possible to synthesize monomeric salt-free Cp^*_2YR complexes in this way (eq 2).

$$\underset{2}{Cp^*_2YCl\cdot THF} + RM \xrightarrow[25\ ^\circ C]{S} Cp^*_2YR + MCl + THF \qquad (2)$$

3: R = $N(SiMe_3)_2$; M = Na; S = toluene
4: R = $CH(SiMe_3)_2$; M = Li; S = Et_2O

Characterization. Compounds 2, 3, and 4 are colorless, extremely air-sensitive, and thermally quite stable compounds. The chloride 2 and the amide 3 are stable to above 250 °C whereas the carbyl 4 decomposes at about 125 °C. Cryoscopy in benzene shows that 2, 3, and 4 are monomeric in solution. The compounds are characterized by the usual spectroscopic techniques (IR, NMR). The IR spectra show the expected Cp* absorptions at 2720 (w), 1490 (m), 1380 (m), 1020 (m), and 800 (w) cm^{-1}. Characteristic $SiMe_3$ bands are found at 1253 (s), 1245 (s), 1000 (s), 870 (s), 775 (m), 750 (m), 665 (m), and 600 (m) cm^{-1} for 3 and at 1250 (s), 1240 (s), 1035 (s), 835 (s), 760 (m), 720 (m), 650 (m), and 590 (m) cm^{-1} in the IR spectrum of 4.

The solution ^1H and ^{13}C NMR spectral data (cf. Experimental Section and Table I) are in agreement with the molecular formulas. The ^1H spectra give both chemical shifts and integrations as expected for 2 and Cp^*_2YR compounds. An aspect worth mentioning here is the presence of a small second-order yttrium coupling ($^2J_{Y-H}$ = 2.3 Hz) on the α-hydrogen of the bis(trimethylsilyl)methyl ligand[39] in 4. In this compound the Cp* resonances are observed as two signals (1:1 ratio) indicating inequivalent Cp* ligands, as expected for a nonplanar α-carbon

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Table III. Final Positional Parameters for the Non-Hydrogen Atoms of $Cp^*_2YN(SiMe_3)_2$ (3) and Equivalent Isotropic Temperature Factor[a]

atom	x	y	z	U_{eq}, Å^2
Molecule 1				
Y(1)	0.41853 (5)	0.74092 (4)	0.10145 (2)	0.0133 (2)
Si(1)	0.6285 (2)	0.7362 (1)	0.02459 (6)	0.0219 (6)
Si(2)	0.7000 (2)	0.7288 (1)	0.11856 (6)	0.0170 (6)
N(1)	0.5959 (4)	0.7347 (3)	0.0757 (2)	0.018 (2)
C(1)	0.4054 (5)	0.5727 (4)	0.0859 (2)	0.015 (2)
C(2)	0.4168 (5)	0.5812 (4)	0.1313 (2)	0.009 (2)
C(3)	0.3131 (6)	0.6186 (4)	0.1434 (2)	0.015 (2)
C(4)	0.2379 (6)	0.6337 (4)	0.1050 (2)	0.020 (2)
C(5)	0.2946 (6)	0.6077 (4)	0.0706 (2)	0.015 (2)
C(6)	0.4903 (6)	0.5275 (4)	0.0614 (2)	0.024 (2)
C(7)	0.5103 (7)	0.5396 (5)	0.1614 (3)	0.023 (2)
C(8)	0.2821 (6)	0.6301 (5)	0.1882 (2)	0.028 (2)
C(9)	0.1072 (7)	0.6523 (5)	0.1025 (3)	0.029 (2)
C(10)	0.2417 (7)	0.6036 (5)	0.0245 (3)	0.031 (2)
C(11)	0.3798 (6)	0.8888 (4)	0.1405 (2)	0.018 (2)
C(12)	0.2653 (6)	0.8598 (4)	0.1264 (2)	0.019 (2)
C(13)	0.2523 (6)	0.8612 (4)	0.0811 (2)	0.022 (2)
C(14)	0.3595 (6)	0.8916 (4)	0.0673 (2)	0.021 (2)
C(15)	0.4372 (6)	0.9092 (4)	0.1042 (2)	0.021 (2)
C(16)	0.4234 (7)	0.9075 (6)	0.1858 (3)	0.032 (2)
C(17)	0.1722 (7)	0.8495 (6)	0.1549 (3)	0.035 (2)
C(18)	0.1413 (7)	0.8502 (5)	0.0518 (3)	0.037 (2)
C(19)	0.3757 (8)	0.9166 (5)	0.0228 (3)	0.036 (2)
C(20)	0.5539 (6)	0.9529 (4)	0.1044 (3)	0.033 (2)
C(21)	0.4942 (7)	0.7197 (6)	−0.0123 (2)	0.034 (2)
C(22)	0.6983 (7)	0.8387 (5)	0.0093 (2)	0.035 (2)
C(23)	0.7358 (8)	0.6524 (6)	0.0132 (3)	0.041 (2)
C(24)	0.8180 (7)	0.8117 (5)	0.1210 (3)	0.032 (2)
C(25)	0.7829 (7)	0.6259 (5)	0.1259 (3)	0.023 (2)
C(26)	0.6232 (6)	0.7466 (5)	0.1679 (2)	0.019 (2)
Molecule 2				
Y(2)	0.10392 (5)	0.23778 (4)	0.16371 (2)	0.0138 (2)
Si(3)	−0.1557 (2)	0.1403 (1)	0.15042 (6)	0.0199 (6)
Si(4)	−0.1683 (2)	0.3331 (1)	0.15757 (7)	0.0207 (6)
N(2)	−0.0937 (4)	0.2386 (3)	0.1581 (2)	0.017 (2)
C(27)	0.0922 (6)	0.2680 (4)	0.0802 (2)	0.015 (2)
C(28)	0.1846 (6)	0.3186 (4)	0.0999 (2)	0.016 (2)
C(29)	0.2782 (6)	0.2639 (4)	0.1153 (2)	0.018 (2)
C(30)	0.2410 (6)	0.1793 (4)	0.1073 (2)	0.023 (2)
C(31)	0.1258 (5)	0.1812 (4)	0.0846 (2)	0.013 (2)
C(32)	−0.0148 (7)	0.2995 (5)	0.0536 (2)	0.025 (2)
C(33)	0.1944 (7)	0.4142 (5)	0.0976 (3)	0.030 (2)
C(34)	0.4022 (6)	0.2959 (5)	0.1287 (3)	0.025 (2)
C(35)	0.3136 (7)	0.0996 (5)	0.1140 (3)	0.030 (2)
C(36)	0.0649 (7)	0.1066 (5)	0.0626 (2)	0.021 (2)
C(37)	0.1347 (6)	0.3042 (4)	0.2426 (2)	0.015 (2)
C(38)	0.2484 (6)	0.3045 (4)	0.2287 (2)	0.016 (2)
C(39)	0.2853 (6)	0.2193 (4)	0.2256 (2)	0.020 (2)
C(40)	0.1938 (6)	0.1650 (4)	0.2366 (2)	0.019 (2)
C(41)	0.1030 (6)	0.2170 (4)	0.2481 (2)	0.017 (2)
C(42)	0.0728 (7)	0.3804 (5)	0.2579 (3)	0.025 (2)
C(43)	0.3194 (6)	0.3845 (5)	0.2251 (3)	0.024 (2)
C(44)	0.4081 (6)	0.1877 (5)	0.2208 (2)	0.025 (2)
C(45)	0.2061 (7)	0.0705 (4)	0.2430 (3)	0.022 (2)
C(46)	−0.0056 (7)	0.1885 (5)	0.2671 (2)	0.024 (2)
C(47)	−0.0326 (7)	0.0609 (5)	0.1603 (2)	0.024 (2)
C(48)	−0.2637 (7)	0.1113 (5)	0.1881 (3)	0.034 (2)
C(49)	−0.2358 (7)	0.1224 (5)	0.0959 (2)	0.025 (2)
C(50)	−0.2520 (7)	0.3482 (5)	0.2054 (3)	0.034 (2)
C(51)	−0.2809 (7)	0.3495 (5)	0.1101 (3)	0.028 (2)
C(52)	−0.0577 (7)	0.4216 (5)	0.1564 (3)	0.026 (2)

[a] Here and in the following tables the number in parentheses is the estimated standard deviation in the least significant digit. U_{eq} = one-third of the trace of the orthogonalized anisotropic temperature factor.

Table IV. Positional Parameters for the Non-Hydrogen Atoms of $Cp^*_2YCH(SiMe_3)_2$ (4)

atom	x	y	z	U_{eq}, Å^2
Y	0.27381 (4)	0.10854 (3)	0.02748 (5)	0.0140 (2)
Si(1)	0.1431 (1)	0.0931 (1)	−0.1321 (1)	0.0193 (6)
Si(2)	0.0809 (1)	0.2009 (1)	−0.0106 (1)	0.0210 (6)
C(1)	0.1588 (4)	0.1525 (3)	−0.0434 (5)	0.015 (2)
C(2)	0.2322 (4)	0.0474 (3)	−0.1419 (5)	0.021 (2)
C(3)	0.0666 (4)	0.0367 (3)	−0.1142 (4)	0.024 (2)
C(4)	0.1232 (4)	0.1261 (3)	−0.2504 (4)	0.027 (2)
C(5)	0.0650 (4)	0.2658 (3)	−0.0938 (5)	0.036 (2)
C(6)	0.0982 (4)	0.2403 (3)	0.1044 (4)	0.027 (2)
C(7)	−0.0111 (4)	0.1617 (3)	−0.0066 (5)	0.028 (2)
C(8)	0.4173 (4)	0.1412 (3)	0.0301 (4)	0.016 (2)
C(9)	0.3951 (3)	0.1342 (3)	−0.0659 (4)	0.014 (2)
C(10)	0.3459 (4)	0.1823 (3)	−0.0860 (4)	0.015 (2)
C(11)	0.3336 (4)	0.2172 (3)	−0.0054 (4)	0.016 (2)
C(12)	0.3796 (4)	0.1907 (3)	0.0647 (4)	0.017 (2)
C(13)	0.4823 (3)	0.1046 (3)	0.0741 (4)	0.025 (2)
C(14)	0.4311 (4)	0.0906 (3)	−0.1306 (4)	0.028 (2)
C(15)	0.3164 (4)	0.1997 (4)	−0.1826 (4)	0.029 (2)
C(16)	0.2908 (4)	0.2750 (3)	−0.0007 (5)	0.029 (2)
C(17)	0.3908 (4)	0.2195 (3)	0.1590 (4)	0.026 (2)
C(18)	0.1880 (4)	0.0470 (3)	0.1421 (4)	0.019 (2)
C(19)	0.2428 (4)	0.0811 (3)	0.1977 (4)	0.015 (2)
C(20)	0.3126 (4)	0.0528 (3)	0.1862 (4)	0.021 (2)
C(21)	0.3033 (4)	0.0061 (3)	0.1209 (4)	0.019 (2)
C(22)	0.2264 (4)	0.0011 (3)	0.0954 (4)	0.021 (2)
C(23)	0.1064 (4)	0.0561 (4)	0.1473 (5)	0.031 (2)
C(24)	0.2247 (4)	0.1307 (3)	0.2674 (4)	0.026 (2)
C(25)	0.3792 (4)	0.0638 (4)	0.2502 (5)	0.034 (2)
C(26)	0.3607 (4)	−0.0390 (3)	0.0933 (5)	0.035 (2)
C(27)	0.1917 (4)	−0.0509 (3)	0.0402 (5)	0.034 (2)

geometry of the R group. The ^{13}C NMR spectra also confirm the molecular formulas and show no unusual features. The chemical shifts of the ring and methyl carbon atoms of the Cp* ligand are at the expected positions (ca. 118 and 12 ppm, respectively) as are the carbon atoms of the trimethylsilyl groups (ca. 5 ppm). In all the compounds Y–C coupling might be expected for the Cp* ring carbon atoms, but this is not observed, indicating that the Cp* ligand is π bonded to the yttrium. On the other hand the methyl carbon of the bis(trimethylsilyl)methyl ligand σ-bonded to yttrium shows a clear coupling to the metal ($^1J_{YC}$ = 36.6 Hz) which is larger than that found in $(Cp_2YMe)_2$[21] of 25.0 Hz where the methyls are in a bridging position but is almost equal to that found in $[Cp_2Y(\eta^2\text{-}CH{=}N\text{-}t\text{-}Bu)]_2$[27] (35.0 Hz).

In contrast to solution spectra solid-state ^{13}C NMR spectra give interesting information on intramolecular interaction between the metal and CH bonds of the R ligands, but discussion of these aspects is postponed (vide infra).

Crystallographic Studies. Low-temperature X-ray diffraction studies of 3 and 4 were carried out, and the results are reported below.

The crystal structure of 3 is composed to two crystallographically independent molecules. Each yttrium atom is bonded to two Cp* ligand in η^5 fashion with the average distances Y(1)–C(η^5) = 2.682 (4) Å and Y(2)–C(η^5) = 2.678 (4) Å (Figures 1 and 2; Table V). The Y–C(η^5) distances observed in 3 (2.632 (7)–2.737 (7) Å) are in the range of values found in other yttrocene organometallics: $[Cp_2YMe]_2$[21] [2.621 (10)–2.683 (11) Å], $[Cp_4Y_2(\mu\text{-}Cl)_2]_n$[22] [2.59 (2)–2.66 (2) Å], $Cp_3Y{\cdot}THF$[23] [2.65(1)–2.766 (7) Å], $[Cp'_2Y(\mu\text{-}H){\cdot}THF]_2$[24] [2.67(1)–2.71 (1) Å], and $Cp^*_2Y(\mu\text{-}Cl)YClCp^*_2$[25] [2.56 (2)–2.69 (2) Å]. In general, the Y–C(η^5)

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distances in monomers do not differ from those in the mentioned dimeric and polymeric compounds. The average metal–ring centroid (Cp^0) distances are Y(1)–Cp^0 = 2.395 (6) Å and Y(2)–Cp^0 = 2.391 (7) Å; the ring centroid metal ring centroid angles are Cp^0(1)–Y(1)–Cp^0(2) = 132.4 (2) and Cp^0(3)–Y(2)–Cp^0(4) = 132.2 (2)°. The triangular environments around both yttrium atoms are completed by nitrogen atoms of bis(trimethylsilyl)amide ligands at distances Y(1)–N(1) = 2.274 (5) Å and Y(2)–N(2) = 2.253 (5) Å. These bond lengths are significantly shorter than those found in $[Cp_2YNCH\text{-}t\text{-}Bu]_2$[26] [2.314 (9) and 2.382 (9) Å] and $[Cp_2Y(\eta^2\text{-}CH{=}N\text{-}t\text{-}Bu)]_2$[27] [2.325 (4) Å]. In their discussion about these Y–N bond distances Evans et al. already noticed that these bonds are much shorter than the expected 2.5 Å. The far shorter Y–N bond in **3** can be explained by assuming a π-dative interaction of b_1 symmetry[28] between the Lewis acid Y and the free electron pair on N. Then **3** will be a 16-electron complex instead of the 14-electron species when the Y–N bond had been a single bond. This explanation is supported by the coplanarity of Y, N, and the silicon atoms. In the Y(1) molecule the N(1) atom is 0.005 (7) Å out of the Y(1),Si(1),Si(2) plane whereas in the Y(2) molecule the displacement out of the Y(2),Si(3),Si(4) plane is 0.048 (8) Å. The striking differences in the molecular geometry of the independent molecules are the bonding angles Y–N–Si. The Y(1) molecules exhibit the extreme value of these bonding angles, Y(1)–N(1)–Si(1) = 129.7 (3)° and Y(1)–N(1)–Si(2) = 107.1 (3)°, whereas in the Y(2) molecule the values are somewhat closer, Y(2)–N(2)–Si(3) = 114.0 (3)° and Y(2)–N(2)–Si(4) = 120.2 (3)°. These close structures at the Si(2) and Si(4) sites are caused by an interaction of the methyl groups C(26) and C(47) with the Y(1) and Y(2) atoms, respectively.

This interaction is best seen at C(26) in molecule 1 with Y(1)···H(262) = 2.45 (6) Å, Y(1)···H(263) = 3.00 (6) Å, and Y(1)···C(26) = 2.970 (6) Å. The bond distances C(26)–H(262) and C(26)–H(263) are 1.00 (6) and 1.04 (6) Å, respectively. A similar interaction is observed in $Yb(NSiMe_3)_2)_2\cdot DMPE$[29] and interpreted as a methyl bridge between the Yb and the Si atoms. However, in **3** the orientation of the interacting C–H bonds, Y(1)–H(262)–C(26) = 110.4 (50)° and Y(1)–H(263)–C(26) = 101.4 (50)°, strongly suggests that the Lewis acid Y interacts with the electron density of both these C–H bonds. Therefore it seems appropriate to describe the interaction as "γ-agostic", adopting the term agostic as proposed by Brookhart and Green.[30] In the Y(2) molecule the Y···H distances are somewhat longer, Y(2)···H(473) = 2.82 (6) Å and Y(2)···H(472) = 3.41 (6) Å.

Bond lengths and angles in the (trimethylsilyl)amine groups of both molecules fall into a narrow range: N(1)–Si(1) = 1.696 (9) Å N(1)–Si(2) = 1.704 (6) Å, N(2)–Si(3) = 1.704 (6) Å, N(2)–Si(4) = 1.710 (6) Å; Si–C distances from 1.843 (8) to 1.892 (7) Å in the molecule of Y(1) and from 1.882 (2) to 1.891 (9) Å in the molecule of Y(2). The bond angles N–Si–C are in the range 107.2 (3)–116.4 (3)° for the Y(1) molecule and 106.4 (3)–115.2 (3)° for the Y(2) molecule. The smallest N–Si–C angles [107.2 (3), 106.4 (3)°] involve the methyl groups of C(26) and C(47), both with short intramolecular Y···H distances. The C–Si–C angles range from 103.8 (4) to 107.9 (4)° in the molecule of Y(1) and from 104.7 (4) to 109.5 (4)° in the molecule of Y(2). The Si–N–Si angles are 123.2 (3) [in the molecule of Y(1)] and 125.6 (3)° [in the molecule of Y(2)]. The relative orientation of two trimethylsilyl groups is approximately eclipsed in both molecules (Figures 1 and 2).

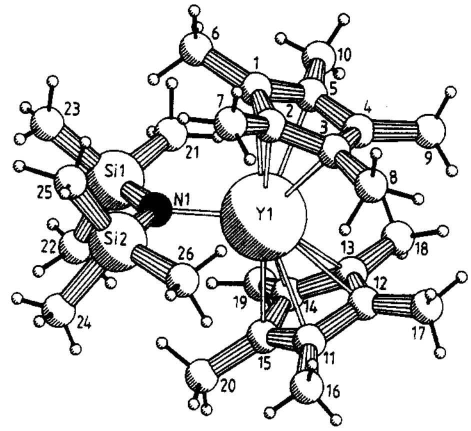

Figure 1. PLUTO drawing of the molecular structure of $Cp^*_2YN(SiMe_3)_2$ (**3**) (molecule 1).

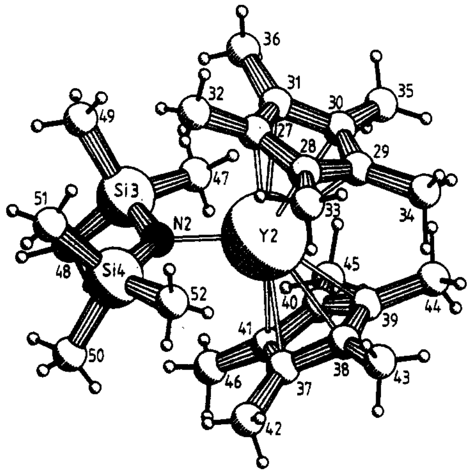

Figure 2. PLUTO drawing of the molecular structure of $Cp^*_2YN(SiMe_3)_2$ (**3**) (molecule 2).

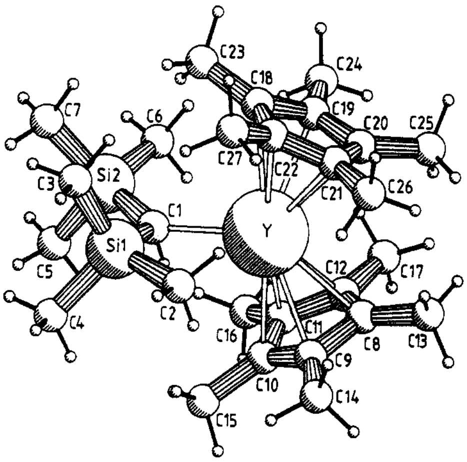

Figure 3. PLUTO drawing of the molecular structure of $Cp^*_2YCH(SiMe_3)_2$ (**4**).

There is no evidence of localization of the π-electron density in the pentamethylcyclopentadienyl rings. The mean value of C···C, 1.416 (10) Å, and bond angles (in the rings), 108.0 (6)°, for both molecules are the same. The mean values of ring to methyl carbon atoms, C–C, are 1.499

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Table V. Selected Interatomic Distances (Å) and Angles for $Cp^*_2YN(SiMe_3)_2$ (3) and $Cp^*_2YCH(SiMe_3)_2$ (4)[a]

molecules					
3 - 1		3 - 2		4	
		(a) Bond Distances			
Cp*(1) [C(1)-C(5)]		Cp*(3) [C(27)-C(31)]		Cp*(1) [C(8)-C(12)]	
⟨Y(1)-C(η^5)⟩	2.677 (4)	⟨Y(2)-C(η^5)⟩	2.666 (4)	⟨Y-C(η^5)⟩	2.668 (4)
Y(1)-Cp^0(1)	2.391 (3)	Y(2)-Cp^0(3)	2.378 (3)	Y-Cp^0(1)	2.382 (3)
$\langle C-C\rangle_{ring}$	1.416 (4)	$\langle C-C\rangle_{ring}$	1.417 (4)	$\langle C-C\rangle_{ring}$	1.412 (4)
$\langle C-CH_3\rangle$	1.505 (5)	$\langle C-CH_3\rangle$	1.502 (5)	$\langle C-CH_3\rangle$	1.514 (4)
Cp*(2) [C(11)-C(14)]		Cp*(4) [C(37)-C(41)]		Cp*(2) [C(18)-C(22)]	
⟨Y(1)-C(η^5)⟩	2.687 (4)	⟨Y(2)-C(η^5)⟩	2.690 (4)	⟨Y-C(η^5)⟩	2.669 (4)
Y(1)-Cp^0(2)	2.400 (4)	Y(2)-Cp^0(4)	2.405 (3)	Y-Cp^0(2)	2.381 (3)
$\langle C-C\rangle_{ring}$	1.419 (4)	$\langle C-C\rangle_{ring}$	1.417 (4)	$\langle C-C\rangle_{ring}$	1.420 (4)
$\langle C-CH_3\rangle$	1.492 (5)	$\langle C-CH_3\rangle$	1.508 (5)	$\langle C-CH_3\rangle$	1.505 (4)
		[Bis(trimethyl)silyl]X Ligand (X = N, C)			
Y(1)-N(1)	2.274 (5)	Y(2)-N(2)	2.253 (5)	Y-C(1)	2.468 (7)
N(1)-Si(1)	1.696 (6)	N(2)-Si(3)	1.704 (5)	C(1)-Si(1)	1.842 (7)
N(1)-Si(2)	1.704 (6)	N(2)-Si(4)	1.710 (5)	C(1)-Si(2)	1.833 (7)
Si(1)-C(21)	1.843 (8)	Si(3)-C(47)	1.882 (8)	Si(1)-C(2)	1.896 (7)
Si(1)-C(22)	1.882 (8)	Si(3)-C(48)	1.866 (9)	Si(1)-C(3)	1.871 (7)
Si(1)-C(23)	1.861 (9)	Si(3)-C(49)	1.879 (8)	Si(1)-C(4)	1.890 (6)
Si(2)-C(24)	1.872 (8)	Si(4)-C(50)	1.891 (9)	Si(2)-C(5)	1.876 (7)
Si(2)-C(25)	1.874 (8)	Si(4)-C(51)	1.884 (9)	Si(2)-C(6)	1.898 (6)
Si(2)-C(26)	1.892 (7)	Si(4)-C(52)	1.883 (8)	Si(2)-C(7)	1.866 (7)
		(b) Bond Angles			
N(1)-Si(1)-C(21)	110.0 (3)	N(2)-Si(3)-C(47)	106.4 (3)	C(1)-Si(1)-C(2)	108.4 (3)
N(1)-Si(1)-C(22)	113.6 (3)	N(2)-Si(3)-C(48)	115.2 (3)	C(1)-Si(1)-C(3)	117.0 (3)
N(1)-Si(1)-C(23)	113.2 (4)	N(2)-Si(3)-C(49)	114.8 (3)	C(1)-Si(1)-C(4)	113.1 (3)
C(21)-Si(1)-C(22)	107.9 (4)	C(47)-Si(3)-C(48)	105.8 (3)	C(2)-Si(1)-C(3)	107.2 (3)
C(21)-Si(1)-C(23)	107.6 (4)	C(47)-Si(3)-C(49)	109.5 (3)	C(2)-Si(1)-C(4)	105.0 (3)
C(22)-Si(1)-C(23)	104.2 (4)	C(48)-Si(3)-C(49)	104.8 (4)	C(3)-Si(1)-C(4)	105.3 (3)
N(1)-Si(2)-C(24)	115.7 (3)	N(2)-Si(4)-C(50)	113.5 (3)	C(1)-Si(2)-C(5)	111.2 (3)
N(1)-Si(2)-C(25)	116.5 (3)	N(2)-Si(4)-C(51)	115.1 (3)	C(1)-Si(2)-C(6)	113.0 (3)
N(1)-Si(2)-C(26)	107.2 (3)	N(2)-Si(4)-C(52)	107.6 (3)	C(1)-Si(2)-C(7)	115.8 (3)
C(24)-Si(2)-C(25)	103.8 (4)	C(50)-Si(4)-C(51)	104.7 (4)	C(5)-Si(2)-C(6)	104.3 (3)
C(24)-Si(2)-C(26)	105.3 (4)	C(50)-Si(4)-C(52)	109.0 (4)	C(5)-Si(2)-C(7)	104.6 (3)
C(25)-Si(2)-C(26)	107.5 (4)	C(51)-Si(4)-C(52)	106.7 (4)	C(6)-Si(2)-C(7)	107.0 (3)
Si(1)-N(1)-Si(2)	123.1 (3)	Si(3)-N(2)-Si(4)	125.6 (3)	Si(1)-C(1)-Si(2)	119.3 (4)
Y(1)-N(1)-Si(1)	129.7 (3)	Y(2)-N(2)-Si(3)	114.0 (3)	Y-C(1)-Si(1)	97.1 (3)
Y(1)-N(1)-Si(2)	107.1 (3)	Y(2)-N(2)-Si(4)	120.2 (3)	Y-C(1)-Si(2)	138.6 (4)
Cp^0(2)-Y(1)-N(1)	112.0 (2)	Cp^0(3)-Y(2)-N(2)	114.6 (2)	Cp^0(1)-Y-C(1)	107.5 (3)
Cp^0(2)-Y(1)-N(1)	114.2 (2)	Cp^0(4)-Y(2)-N(2)	113.1 (2)	Cp^0(2)-Y-C(1)	114.6 (3)
Cp^0(1)-Y(1)-Cp(2)	132.4 (2)	Cp^0(3)-Y(2)-Cp^0(4)	132.2 (2)	Cp^0(1)-Y-Cp^0(2)	134.4 (4)

[a] Cp^0 = ring centroid.

(10) and 1.505 (10) Å in the Y(1) and Y(2) molecules, respectively. All four pentamethylcyclopentadienyl rings are "dished"; methyl carbon atoms lie out of the plane [displacements being in the range from 0.11 (4) to 0.36 (4) Å], exo to the metal atoms. This effect was observed in peralkylated species as $Cp^*_2TiCl_2$[31,32] and $C_5Me_4EtTiCl_3$[33] and also in the partly alkylated $[Cp'_2Y(\mu\text{-}H)\cdot THF]_2$.[24]

The crystal structure of 4 is composed of only one molecule in which the yttrium atom is bonded to the two Cp* ligands in a η^5 fashion (Figure 3). The Y-C(η^5) distances are as in 3 (2.637 (6)-2.692 (6) Å (Table V), average 2.668 (7) Å) normal for yttrocene organometallics (vide supra). The ring centroid-metal-ring centroid angle is 134.4 (4)°.

The Y-C(1) bond length of 2.468 (7) Å is shorter than the known Y-C distances in the dimeric $[Cp_2YMe]_2$,[21] 2.552 (10) and 2.537 (9) Å, and $[Cp_2Y(\eta^2\text{-}CH{=}N\text{-}t\text{-}Bu)]_2$[27] complexes, 2.545 (5) and 2.561 (5) Å, in which the C atoms are in bridging positions. This shortening of about 0.1 Å is quite normal going from bridging to nonbridging.[34] The C(1) atom of the bis(trimethylsilyl)methyl ligand has no free electron pair like the N atom of the amide in 3. The Lewis acidity of the yttrium atom here leads to an "α-agostic"[30] interaction between Y and the C(1)-H(1) bond. This interaction is expressed by the Y-C(1)-H(1) angle of 84 (3)° and the Y···H(1) distance of 2.53 (6) Å. There is no coplanarity of the Y, C(1), and the silicon atoms. The C(1) atom is 0.248 (8) Å out of the Y, Si(1), and Si(2) plane. In addition to this 4 displays an interaction between a methyl group (C2) of the carbyl ligand and the Y atom quite analogous to that observed in 3 (vide supra). However, the distances Y···C(2), 2.878 (7) Å, Y···H(22), 2.45 (5) Å, and Y···H(23), 3.00 (5) Å, are shorter than in 3, which indicates that the "γ-agostic" interaction between yttrium and a methyl group is stronger in 4 than in 3. It suggests that the π-Y-N interaction in 3 is more effective in reducing the electron deficiency on the metal atom than the "α-agostic Y···C-H bond" in 4. The environment of the C(1) atom is completed by the silicon atoms of the two

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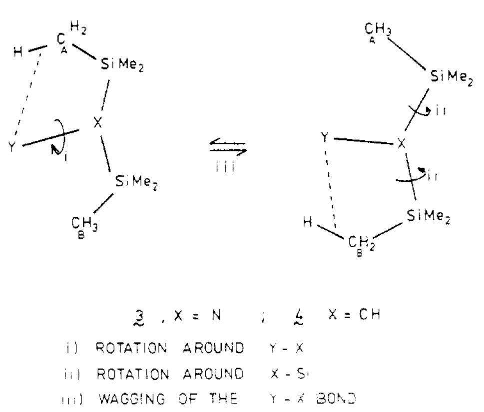
(34) (a) The Al-C bond lengths in $Cp_2Y(\mu\text{-}Me)_2AlMe_2$ are 2.10 Å for the bridging and 1.98 Å for the terminal methyl group, giving a difference of 0.12 Å. Scollary, G. R. *Aust. J. Chem.* **1978**, *31*, 411-414. (b) In $Mg(Al(Me)_4)_2$, Al-μ-C = 2.10 Å and Al-C = 1.96 Å. The difference is 0.14 Å. Atwood, J. L.; Stucky, G. P. *J. Am. Chem. Soc.* **1969**, *91*, 2538-2543.

Scheme I



trimethylsilyl groups. The bond lengths C(1)–Si(1) of 1.842 (7) Å and C(1)–Si(2) of 1.833 (7) Å are significantly shorter than the other Si–C distances which vary from 1.866 (7) to 1.898 (6) Å. The Y–C(1)–Si(1) angle of 97.1 (3)° and the Y–C(1)–Si(2) angle of 138.6 (4)° are remarkable and caused by the agostic interactions. The magnitude of the angles is comparable with those found in $Cp*_2NdCH(SiMe_3)_2$[12] of 98.4 (3) and 140.2 (4)°, respectively. The Si(1)–C(1)–Si(2) angle of 119.3 (4)° is also comparable with the Nd compound (121.3 (4)°). The displacement α in the *yz* plane as defined by Lauher and Hoffmann for metallocene complexes[28] is 22.0 (4)°.

Analogous to **3**, the Cp* ligands of **4** have their methyl groups also dished out of the plane (displacements are in the range of 0.12 (2)–0.37 (3) Å).

The structures of **3** and **4** irrefutably show the presence of agostic Y···CH interactions. Furthermore it is remarkable that besides the γ interaction, present in **3** and **4**, the carbyl **4** also has an α-agostic interaction. Normally these interactions manifest themselves in IR and NMR spectra.[30] IR spectra usually show low-energy C–H stretching vibrations in the range of 2700–2350 cm^{-1}. In our complexes these characteristic absorptions are not observed. It is clear that IR spectroscopy is not a reliable diagnostic tool for finding agostic M···CH interactions in a molecule. In NMR spectra of complexes with static agostic M···CH interactions quite low values of the coupling constants $^1J_{CH}$ are observed, for sp^3 CH bonds in the range of 75–100 Hz.[30] Indeed the solution ^{13}C NMR spectrum of **4** displays the characteristically small $^1J_{CH}$ (84.2 Hz) which is clearly associated with the α-CH resonance of the $CH(SiMe_3)_2$ ligand (Table I). The γ-agostic interactions of the methyl group of the $SiMe_3$ fragments in **3** and **4** are not reflected in low $^1J_{CH}$ values. The observed data (116.0 Hz for **3** and 116.6 Hz for **4**) are almost identical with the $^1J_{CH}$ (118.0 Hz) value for $SiMe_4$.[35] It is very like that a fast fluxional process in which all methyl groups in turn form γ-agostic interactions leads to an averaged $^1J_{CH}$ value very close to that of a noninteracting $SiMe_3$ group.[36] This dynamic agostic Y···CH interaction is also responsible for the observation that solution ^1H and ^{13}C NMR spectra only show equivalent $SiMe_3$ groups.

Such a dynamic process can be explained by assuming one (or a combination) of the following mechanisms[37] (Scheme I). Rotation around the Y–X bonds (i) is very unlikely since in **4** two Cp* resonances are present in the solution ^1H and ^{13}C spectra.[38] In addition, the presence of a static "α-agostic" Y···CH bond strongly favors a rigid Y–X bond as well as the π-interaction in **3**. The possibilities ii and iii represent processes that will work simultaneously under the conditions of the NMR experiments. Mere rotation (possibility ii) is not sufficient to account for the experimental observations since two $SiMe_3$ resonances (in 1:1 ratio) would be expected then. A static system in which this rotation does not occur would give a three-resonance spectrum (1:2:3 ratio). In the solid state the wagging process (possibility iii) appears to be inoperative, and only rotation around X–Si (possibility ii) remains. In the solid-state ^{13}C NMR of **3** two $SiMe_3$ signals (1:1 ratio) at 6.6 and 13.8 ppm are observed. The low-field resonance is assigned to the $SiMe_3$ group undergoing the interaction with the metal atom. Compared with the solution spectra it experiences an extra deshielding influence. It is interesting to notice that in **3** in the solid state the barrier for rotation around the N–Si bond at room temperature is still quite low, despite the distinct interaction between the yttrium atom and one of the methyl groups as indicated in the structure. The solid-state ^{13}C NMR spectrum of **4** shows three clear resonances in the region of interest (0–15 ppm) with an intensity ratio 11:3:2. One methyl carbon coincides with the Cp* resonance at 13.5 ppm. The methyl intensity ratio of the trimethylsilyl groups is therefore 1:3:2, exactly as expected for the situation in which the Y···Me interaction becomes "static". This means that in **4** the Y···Me interaction is strong enough to suppress rotation around the X–Si bond (possibility ii) in the interacting $SiMe_3$ moiety. It also confirms that this interaction is stronger in **4** than in **3** in full agreement with the X-ray structures (vide supra). The position of the resonance of the free $SiMe_3$ group (δ 7.8) supports the assignment for the $SiMe_3$ signals in **3**. The two fixed methyls that have no interaction with yttrium are found at δ 4.2. The NMR observations discussed here enable us to formulate a relative order for the respective activation energies for the averaging processes (Scheme I) as

$$E_a(\mathrm{i}) >> E_a(\mathrm{iii}) > E_a\ (\mathrm{i})$$

From this study it is clear that solid-state NMR spectroscopy is a valuable technique for studying dynamic intramolecular interaction processes since fluxional behavior seems to be, either partially (**3**) or completely (**4**), frozen into a static situation in the solid state. Variable-temperature solid-state NMR measurements currently in progress should further confirm these conclusions.

Conclusions

Monomeric $Cp*_2YR$ compounds are accessible by using the steric bulky ligands R. In these formally 14-electron systems the yttrium atom is coordinatively unsaturated causing a pronounced Lewis acidic behavior leading to intramolecular interactions with bonding or free electron

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(35) Strothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York and London, 1972; p 337.

(36) According to Green[30] the $^1J_{CH}$ of a fluxional system can only be observed as the average of all $^1J_{CH}$ involved. In our case there are 18 C–H bonds of which one interacts. The other 17 are free leading to a $^1J_{CH}$(av) = (17 × 118 + 84)/18 = 116.1 Hz. In the case of only 9 this would have been $^1J_{CH}$(av) = 114.2 Hz.

(37) The rotation around the Si–C bond of the $SiMe_3$ moieties is omitted from the discussion as it unquestionably takes place.

(38) The ^1H NMR spectrum of **4** at 100 °C also shows the two Cp* resonances.

(39) **Note Added in Proof.** After submission of our paper a related yttrium organometallic anion, $[Cp_2Y(CH_2SiMe_3)_2]^-$, was reported: Evans, W. J.; Dominguez, R.; Levan, K. R.; Doedens, R. J. *Organometallics* **1985**, *4*, 1836–1841. This species also shows $^2J_{YH}$ between the metal and methylene protons of the alkyl ligand, but the values given are confusing. Two sets of data are reported; i.e., δ −0.87 ($^2J_{YH}$ = 2.8 Hz) and −0.91 ($^2J_{YH}$ = 6.8 Hz). The first is very close to the value we report here. The second is much larger, indicating substantially stronger interaction between the nuclei. Unfortunately the paper gives no reason or explanation for this discrepancy.

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pairs. In the amide **3**, the free electron pair on the N atom is donated to the metal leading to a short Y–N bond which can be regarded as virtually a double bond. In the carbyl **4**, the electron deficiency of the Y atom causes the formation of an "α-agostic Y···CH interaction". Due to these interactions the systems can be seen as effectively 16-electron systems. The remaining electron deficiency of the yttrium atom in both compounds is decreased by an additional intramolecular "γ-agostic Y···CH interaction" between the yttrium atom and the methyl groups of the amide or carbyl ligands, respectively, as can be clearly seen in the X-ray structure as well as in the solid-state ^{13}C NMR spectra.

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Registry No. **1**, 40585-51-1; **2**, 94348-90-0; **3**, 102829-91-4; **4**, 95197-83-4; Cp*H, 41539-64-4; $YCl_3 \cdot 3THF$, 84147-94-4; $NaN(SiMe_3)_2$, 1070-89-9; $LiCH(SiMe_3)_2$, 41823-71-6.

Supplementary Material Available: Tables of positional and thermal parameters for all atoms and observed and calculated structure factors, a complete list of bond lengths and angles, and the ORTEP drawings of the three molecules (96 pages). Ordering information is given on any current masthead page.

Reactivity of Alkynes toward η^2-CX_2 (X = S, Se) Metal Complexes. 1. The [2 + 2] Condensation of an Alkyne on a Metal Carbene: An Experimental and Theoretical Study. 2. Formation and X-ray Structure of Unusual Doubly and Triply Condensed Cyclic Systems

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The reaction of $(triphos)RhCl(\eta^2\text{-}CX_2)$ [X = S (**1**), X = Se (**2**); triphos = $CH_3C(CH_2PPh_2)_3$] with $(CF_3)C{\equiv}C(CF_3)$ leads to the formation of two new complexes of formula $(triphos)ClRhC(CF_3){=}C(CF_3)CXC(CF_3){=}C(CF_3)X$ (**3** and **4**), containing a metallacyclobutene unit. The salient structural features of **3** have been ascertained by an X-ray structural study: hexagonal; $P6_1$; a = 23.425 (6) Å, c = 18.982 (5) Å; R = 0.063, R_w = 0.060 for 1334 reflections with $I \geq 3\sigma(I)$. A d^8-(triphos)RhCl fragment of the ML_4 type is linked to a chelating $C(CF_3){=}C(CF_3)CS_2C_2(CF_3)_2$ ligand. The four-membered metallacyclobutene ring may result from the addition of an alkyne molecule to the Rh═C linkage of the carbenoid complex $(triphos)ClRh{=}CSC(CF_3){=}C(CF_3)S$. By reaction with Ag$^+$ or Tl$^+$, Cl$^-$ is abstracted from **3** and **4** to give the products $[(triphos)RhC(CF_3){=}C(CF_3)CXC(CF_3){=}C(CF_3)X]BPh_4$ (**5** and **6**). Eventually **3** and **4** can be regenerated from **5** and **6** by treatment with chloride anions. The crystal structure of **5** has been determined: monoclinic; $P2_1/a$; a = 38.649 (10) Å, b = 12.281 (4) Å, c = 14.643 (4) Å, β = 97.64 (2)°; R = 0.061, R_w = 0.061 for 5294 reflections with $I \geq 3\sigma(I)$. With respect to **3**, one sulfur atom of the five-membered 1,3-dithiol ring replaces the chloride ligand in the coordination of rhodium, thus restoring the original η^2-bonding mode of one C–S linkage as in the parent compounds **1**. An unusual feature of **5** and **6** is that one three-, one four-, and one five-membered ring are all condensed and share an unique carbon atom. The problem of the addition of an alkyne to a M═C (metal–carbene) double bond is analyzed theoretically. Explanations are offered why this type of 2 + 2 cycloaddition, formally symmetry forbidden in organic chemistry, becomes allowed for organometallic reactions which lead to the formation of a metallacycle ring.

Introduction

The 1,3-dipole character of heteroallene molecules of the type X═C═Y (X, Y = S, NR) is enhanced by η^2-coordination to metal centers. Alkynes with electron-withdrawing substituents are known to react under mild conditions with η^2-CS_2[2] or η^2-SCNR (R = CH_3, C_2H_5)[3] metal complexes to give 1,3-dithiol-2-ylidene (A) or 1,3-thiazol-2-ylidene (B) derivatives, as shown in 1.

Both the dithiocarbenes of type A and the thiazacarbenes of type B have found useful applications in the synthesis of 1,3-dithiole-2-thiones[3] 1,3-thiazole-2-thiones[3] and substituted tetrathiafulvalenes.[2a–d,4]

With the aim of synthesizing new dithiocarbene deriv-

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