Compound 7b: IR (KBr) $\nu_{C=O}$ 1715 (vs) cm^{-1}; ^1H NMR (CD_3CN) 8.49 (td, 1 H, H_p, $^3J_{H_m-H_p}$ = 9.3 Hz), 8.33 (dd, 1 H, H_o, $^3J_{H_o-H_m}$ = 6.8 Hz), 8.19 (d, 1 H, $H_{m'}$, $^3J_{H_{m'}-H_p}$ = 8.3 Hz), 4.68 and 4.23 (2d, 2 H, CH_2, $^2J_{H_A-H_B}$ = 1.38 Hz), 4.06 (m, 2 H, OCH_2, AB X_3 spin system), 0.92 ppm (t, 3 H, CH_3). Anal. Calcd for $C_{23}H_{20}I_3NO_2Pd$: C, 33.30; H, 2.43; N, 1.69. Found: C, 33.45; H, 2.06; N, 1.63.

Collection of X-ray Data and Structure Determination. Cell constants and other pertinent data are presented in Table VIII for compounds **3″a**, **4a**, and **6**. Intensity data were collected on a Nonius CAD4 diffractometer. Corrections for Lorentz and polarization effects were applied but not for absorption, owing to the low value of the linear absorption coefficient.

The structures were solved on a PDP 11-60 computer with the Enraf-Nonius package.[8] The atomic positions of the independent atoms of the molecules were found with program MULTAN and subsequent Fourier difference synthesis.

For compounds **4a** and **6**, after the refinement of the coordinates and thermal parameters, first isotropic and then anisotropic of the non-hydrogen atoms, the positions of the hydrogen atoms were calculated. Their introduction into the refinement with fixed coordinates and isotropic thermal parameters of 5 $Å^2$ was significant, leading to the R and R_ω values given in Table VIII after the two last cycles of refinement of coordinates and anisotropic thermal parameters of the non-hydrogen atoms.

For compound **3″a**, after the refinement of coordinates and isotropic thermal parameters a Fourier difference synthesis revealed residual peaks assigned to two molecules of solvent, dichloromethane and toluene, respectively. Best refinement was obtained with 0.5 molecule of CH_2Cl_2 and 0.5 molecule of $C_6H_5CH_3$ per asymmetric unit. For the dichloromethane molecule, the atom C12 was placed in general position 8f of the space group $C2/c$ and C30, with an occupancy factor of 0.5, in particular position 4e. The toluene molecule is statistically distributed over two sites related by an inversion center at $^1/_4$, $^3/_4$, $^1/_2$ giving only five independent carbon atoms: C31 and C33 with occupancy factors of 1 and C32, C34, and C35 with occupancy factors of 0.5. Because of this order the hydrogen atoms were not introduced into the refinement. Refinement of the coordinates and thermal parameters (anisotropic for the 37 atoms of compound **3″a** including C12 and C30 and isotropic for C31 to C35) led to the final values of R and R_ω given in Table VIII.

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Registry No. **1**, 105369-55-9; **1***, 109996-96-5; **1****, 109997-17-3; **2a**, 109996-97-6; **2a***, 109997-18-4; **2b**, 109996-98-7; **2c**, 109996-99-8; **2d**, 105784-29-0; **2d****, 109997-15-1; **2e**, 110044-15-0; **2e****, 109997-14-0; **2f**, 109997-00-4; **3a**, 109997-01-5; **3′a**, 109997-13-9; **3″a**, 109997-19-5; **3b**, 109997-02-6; **3c**, 109997-03-7; **3d**, 105813-62-5; **3e**, 105813-63-6; **3f**, 109997-04-8; **4a**, 105784-31-4; **4a***, 109997-20-8; **4b**, 110013-97-3; **4c**, 109997-05-9; **4d**, 109997-06-0; **4e**, 109997-07-1; **4f**, 109997-08-2; **4g**, 109997-09-3; **5a**, 105784-32-5; **5a***, 110013-98-4; **6**, 109997-11-7; **7a**, 109997-12-8; **7b**, 109997-22-0; **8a**, 109978-95-2; **8′a**, 109978-97-4; PhC≡CCO_2Et, 2216-94-6; PhC≡CCO_2Me, 4891-38-7; MeC≡CPh, 673-32-5; PhC≡CPh, 501-65-5; MeOCOC≡CCO_2Me, 762-42-5; MeC≡CMe, 503-17-3.

Supplementary Material Available: Tables of thermal parameters, bond distances and angles including all atoms, and least-squares planes for **3″a**, **4a**, and **6** (17 pages); listings of observed and calculated structure factors for **3″a**, **4a**, and **6** (87 pages). Ordering information is given on any current masthead page.

Reactions of Yttrium–Carbon Bonds with Active Hydrogen-Containing Molecules. A Useful Synthetic Method for Permethylyttrocene Derivatives

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Reactions of the permethylyttrocene compounds $Cp^*_2YCH(SiMe_3)_2$ (**1**) and $Cp^*_2YMe\cdot THF$ (**2**) with a variety of active hydrogen-containing substrates are reported. With HCl the known complexes $(Cp^*_2YCl)_2$ and $Cp^*_2YCl\cdot THF$ are formed. Reaction with 2,4-pentadione gives $Cp^*_2Y(acac)$ (**3**). Alcoholysis of **1** in Et_2O gives alkoxides $Cp^*_2YOR\cdot OEt_2$ (**4**, R = Me; **5**, R = Et; **6**, R = *i*-Pr). In the reactions with α-alkynes alkynyl complexes $Cp^*_2YC{\equiv}CR\cdot OEt_2$ (**7a**, R = Me; **8**, R = Ph; **9**, R = $SiMe_3$) are formed. When **2** reacts with propyne, $Cp^*_2YC{\equiv}CMe\cdot THF$ (**7b**) is isolated. Reaction of **1** with excess of α-alkynes in nonpolar solvents shows a regioselective, catalytic dimerization to 1-en-3-ynes. Both **1** and **2** metalate pyridines at the α-position to give $Cp^*_2Y(\eta^2\text{-}NC_5H_4)$ (**13**) from **1** and $Cp^*_2Y(\eta^2\text{-}NC_5H_4)\cdot THF$ (**14**) and $Cp^*_2Y(\eta^2\text{-}NC_5H_3,6\text{-}Me)$ (**15**) from **2**. Thermolysis of **1** in mesitylene gives the complex Cp^*_2YDMB[1] (**16**), which reacts with THF to form $Cp^*_2YDMB\cdot THF$ (**17**). The hydrides $(Cp^*_2YH)_2$ (**18**) and $Cp^*_2YH\cdot THF$ (**19**) are synthesized by hydrogenolysis of **1** and **2**, respectively. The hydride **19** is a catalyst in H/D exchange reactions between sp^3-CH and sp^2-CD bonds.

Introduction

The last decade has shown a dramatic and interesting development of the organometallic chemistry of group 3 and 4f elements.[2]

We recently reported the synthesis of the new monomeric permethylyttrocenes[1] $Cp^*_2YCH(SiMe_3)_2$ (**1**)[3] and $Cp^*_2YMe\cdot THF$ (**2**).[4] The main objective of these synthetic

(1) In this paper the following abbreviations are used: Cp = η^5-C_5H_5; Cp′ = η^5-C_5H_4Me; Cp* = η^5-C_5Me_5; Fv* = η^1,η^5-$C_5Me_4CH_2$; DMB = η^1-3,5-dimethylbenzyl.

(2) For recent reviews see, for example: (a) Schumann, H. *Angew. Chem.* **1984**, *96*, 493. (b) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*. (c) Watson, P. L.; Parshal, G. W. *Acc. Chem. Res.* **1985**, *18*, 51.

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activities was to prepare well-defined, monomeric σ-YC bond containing yttrocene derivatives.

During our work on Cp_2TiR complexes and their permethyl analogues Cp^*_2TiR[5] we discovered a surprising reactivity of the σ-TiC bond toward molecules with active hydrogen. As examples we mention the metalation of methyl-substituted pyridines by Cp_2TiMe[6] and the hydrogen abstractions of Cp* ligands in Cp^*_2TiR complexes.[7] The coordinative unsaturation of these 15-electron systems is crucial with respect to this reactivity.

It was anticipated that 14-electron systems Cp^*_2YR would show a related and possibly even more exciting behavior. Watson[8] already demonstrated the activity of $(Cp^*_2YMe)_2$ in the CH bond activation of alkanes. These considerations led us to study reactions of **1** and **2** with "active CH bonds". These bonds vary in hybridization from sp to sp^2 to sp^3. Other substrates included in this study were alcohols, HCl, and H_2. We here present the results of these investigations.

Experimental Section

All compounds are extremely air-sensitive. Manipulations were therefore carried out under nitrogen by using glovebox (Braun MB-200), vacuum line/Töpler pump, and Schlenk-line techniques.

NMR spectra were recorded on Nicolet NT200 and Bruker WH-90 spectrometers. IR spectra (KBr/Nujol) were obtained by using a Pye Unicam SP3-300 spectrophotometer. Elemental analyses were carried out by the Micro Analytical Group of the Chemical Laboratories of this University under supervision of Mr. A. F. Hamminga.

$Cp^*_2YCH(SiMe_3)_2$ (**1**)[3] and $Cp^*_2YMe\cdot THF$ (**2**)[4] were prepared as reported earlier. Gases (Matheson C.P.) were used as purchased. Alcohols were distilled from CaO, pyridines from KOH, and mesitylene from Na wire. Phenylethyne, $HC{\equiv}CSiMe_3$, and other liquid substrates were stored on molecular sieves (3 Å) under nitrogen. Solvents (pentane, Et_2O, THF, benzene, toluene) were predried on Na wire and distilled from Na/K alloy benzophenone prior to use.

$(Cp^*_2YCl)_2$. A solution of 0.17 g of **1** (0.32 mmol) in 10 mL of benzene was exposed at room temperature to 0.43 mmol of HCl. After the solution was stirred for 3 h, 0.11 mmol of HCl was recovered. The solvent was removed in vacuo and the white solid washed with pentane. Yield: 0.11 g of $(Cp^*_2YCl)_2$ (0.12 mmol, 75%). IR and ^1H NMR spectra were similar to those reported previously.[9] The $CH_2(SiMe_3)_2$ formed was identified by GC and ^1H NMR ($CDCl_3$, 25 °C): δ −0.35 (s, 2 H, CH_2), 0.06 (s, 18 H, $SiMe_3$).

$Cp^*_2YCl\cdot THF$. A solution of 0.11 g of **2** (0.24 mmol) in 5 mL of toluene was reacted with 0.24 mmol of HCl. After 1 h 0.22 mmol of CH_4 (GC, 93%) was recovered. The toluene was pumped off and the white solid washed with pentane. The IR and ^1H NMR spectra were identical with those of authentic $Cp^*_2YCl\cdot THF$.[3]

$Cp^*_2Y(acac)$ (3). To a solution of 1.61 g of **1** (3.09 mmol) in 35 mL of Et_2O was added at room temperature 0.32 mL of 2,4-pentadione (3.10 mmol). The mixture was stirred for 1 h. After removal of the solvent in vacuo the remaining solid was dissolved in 30 mL of pentane. This solution was stored at −80 °C, and yellow crystals separated. Isolated yield: 0.61 g of **3** (1.31 mmol, 43%). IR (cm^{-1}): 3080 (m), 2720 (w), 1580 (s), 1515 (s), 1490 (m), 1390 (s), 1365 (m), 1265 (m), 1195 (w), 1020 (m), 800 (w), 775 (m), 655 (m), 595 (w), 545 (m), 420 (m), 405 (m). Anal. Calcd for $C_{25}H_{37}YO_2$: C, 65.49; H, 8.13; Y, 19.39. Found: C, 65.71; H, 8.11; Y, 19.43.

$Cp^*_2YOMe\cdot OEt_2$ (4). The procedure was similar to that for **3** with 1.06 g of **1** (2.04 mmol) and 83 μL of methanol. Isolated yield: 0.09 g of **4** (0.20 mmol, 10%) as colorless crystals. IR (cm^{-1}): 2770 (m), 2720 (w), 1485 (m), 1365 (m), 1155 (s), 1090 (m), 1045 (m), 1020 (m), 1000 (m), 890 (w), 870 (w), 800 (w), 780 (m), 595 (w), 505 (w), 420 (m). Anal. Calcd for $C_{25}H_{43}YO_2$: C, 64.64; H, 9.44. Found: C, 64.56; H, 9.44.

$Cp^*_2YOEt\cdot OEt_2$ (5). Starting with 0.66 g of **1** (1.26 mmol) and 74 μL of ethanol 0.40 g of **5** (0.83 mmol, 65%) was isolated as colorless crystals. IR (cm^{-1}): 2720 (w), 2690 (w), 1490 (m), 1365 (m), 1325 (w), 1260 (m), 1145 (s), 1085 (m), 1085 (m), 1040 (m), 1020 (m), 1000 (m), 900 (m), 855 (m), 820 (w), 800 (w), 770 (w), 590 (w), 495 (m). Anal. Calcd for $C_{26}H_{45}YO_2$: C, 65.26; H, 9.48. Found: C, 64.97; H, 9.45.

$Cp^*_2YO\text{-}i\text{-}Pr\cdot OEt_2$ (6). To a solution of 0.90 g of **1** (1.74 mmol) in 20 mL of Et_2O was added at room temperature 0.13 mL of 2-propanol, and the mixture was stirred for 26 h. After workup identical as described for **3** 0.23 g of **6** (0.47 mmol, 27%) was isolated as pale yellow crystals. IR (cm^{-1}): 2720 (w), 2610 (w), 1490 (m), 1390 (m), 1365 (m), 1330 (m), 1290 (w), 1190 (w), 1160 (s), 1135 (m), 1115 (w), 1090 (w), 1045 (m), 1020 (m), 995 (s), 895 (m), 835 (m), 800 (w), 775 (m), 595 (w), 530 (m), 455 (m), 435 (m). Anal. Calcd for $C_{27}H_{47}YO_2$: C, 65.48; H, 9.62. Found: C, 65.87; H, 9.67.

$Cp^*_2YC{\equiv}CMe\cdot OEt_2$ (7a). A solution of 1.00 g of **1** (1.93 mmol) in 15 mL of Et_2O was exposed to 1.95 mmol of propyne and stirred for 2 h at room temperature. The solvent and $CH_2(SiMe_3)_2$ (^1H NMR) were pumped off, and the remaining solid was extracted with pentane. Crystallization at −80 °C afforded 0.35 g of **7a** (0.75 mmol, 38%) as colorless crystals (yield 48%). IR (cm^{-1}): 2720 (w), 2075 (m), 1480 (m), 1430 (s), 1365 (m), 1320 (w), 1290 (w), 1190 (m), 1145 (s), 1090 (m), 1045 (m), 1020 (m), 1000 (s), 950 (m), 895 (m), 830 (m), 795 (w), 775 (m), 590 (w), 520 (m), 360 (m). Anal. Calcd for $C_{27}H_{43}YO$: C, 68.63; H, 9.17. Found: C, 68.43; H, 9.17.

$Cp^*_2YC{\equiv}CMe\cdot THF$ (7b). In a NMR tube 0.025 mmol of propyne was condensed onto a solution of 11 mg of **2** (0.025 mmol) in 0.4 mL of C_6D_6 at −196 °C, and the tube was sealed. After the tube was warmed to room temperature, the ^1H NMR spectrum was recorded (Table I). The solvent was evaporated and the IR spectrum of the white solid taken. IR (cm^{-1}): 2720 (w), 2080 (m), 1480 (m), 1360 (m), 1340 (m), 1295 (w), 1235 (w), 1175 (w), 1085 (m), 1050 (m), 1020 (s), 955 (s), 915 (w), 860 (m), 810 (m), 800 (w), 665 (s), 615 (w), 595 (w), 375 (m).

$Cp^*_2YC{\equiv}CPh\cdot OEt_2$ (8). A solution of 0.58 g of **1** (1.12 mmol) in 25 mL of Et_2O was treated with 0.12 mL of phenylethyne (1.12 mmol) and stirred for 4 h. After workup and crystallization from 15 mL of pentane at −80 °C, 0.26 g of **8** was isolated as off-white crystals, yield 48%. IR (cm^{-1}): 3060 (w), 2720 (w), 2065 (w), 1590 (m), 1570 (m), 1480 (m), 1365 (m), 1290 (w), 1245 (w), 1200 (m), 1190 (m), 1090 (m), 1040 (s), 1020 (m), 1000 (m), 910 (m), 895 (m), 840 (w), 830 (w), 795 (w), 785 (s), 765 (s), 690 (s), 590 (w), 535 (w), 520 (m), 470 (m), 320 (m). Anal. Calcd for $C_{35}H_{45}YO$: C, 71.89; H, 8.48. Found: C, 71.64; H, 8.53.

$Cp^*_2YC{\equiv}CSiMe_3\cdot OEt_2$ (9). To a solution of 0.53 g of **1** (1.02 mmol) in 15 mL of Et_2O was added at room temperature 0.14 mL of $HC{\equiv}CSiMe_3$ (1.02 mmol), and the mixture was stirred for 4 h. After the solvent was evaporated, the solid was extracted with 4 mL of pentane. The clear solution was stored overnight at −80 °C, and the colorless crystals formed were filtered off and isolated. Yield: 0.20 g of **9** (0.43 mmol, 41%). IR (cm^{-1}): 2720 (w), 2080 (m), 1480 (m), 1365 (m), 1245 (s), 1190 (w), 1130 (w), 1090 (m), 1055 (m), 1020 (m), 1000 (m), 895 (w), 860 (s), 840 (s), 795 (w), 775 (m), 760 (m), 680 (s), 595 (w), 325 (m).

Catalytic Dimerization of α-Alkynes by 1. 2-Methyl-1-penten-3-yne (10). A solution of 42 mg of **1** (0.08 mmol) in 15 mL of benzene was exposed to 204 mmol of propyne at room temperature, and a smooth reaction started, which consumed all propyne in 3 h. The product and the solvent were distilled off. The remaining solid was studied by ^1H NMR and IR and identified as $Cp^*_2YC{\equiv}CMe$ (**7c**). IR (cm^{-1}): 2720 (w), 2070 (m), 1485 (m), 1365 (m), 1330 (m), 1255 (m), 1150 (m), 1095 (s), 1070 (m), 1025 (m), 995 (w), 815 (s), 800 (w), 620 (m), 590 (m), 550 (m), 430

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Table I. ^{1}H NMR Data[a] of the New Permethylttrocene Derivatives

complex	Cp*	R	L
3	1.94 (s, 30 H)	1.76 (s, 6 H, C*Me*), 5.13 (s, 1 H, C*H*)	
4	2.02 (s, 30 H)	3.98 (s, 3 H, O*Me*)	0.86 (t, 6 H, J = 7.03, β-Et), 3.32 (q, 4 H, α-Et)
5	2.02 (s, 30 H)	1.30 (t, 3 H, J = 6.70, β-Et), 4.19 (q, 2 H, α-Et)	0.86 (t, 6 H, J = 7.03, β-Et), 3.36 (q, 4 H, α-Et)
6	2.02 (s, 30 H)	1.26 (d, 6 H, J = 5.90, CMe_2), 4.66 (m, 1 H, OC*H*)	0.93 (t, 6 H, J = 7.02, β-Et), 3.44 (q, 4 H, α-Et)
7a	2.12 (s, 30 H)	1.95 (s, 3 H, CC*Me*)	0.93 (t, 6 H, J = 7.03, β-Et), 3.41 (q, 4 H, α-Et)
7b	2.11 (s, 30 H)	2.00 (s, 3 H, CC*Me*)	1.20 (m, 4 H, β-THF), 3.57 (m, 4 H, α-THF)
7c	2.02 (s, 30 H)	1.78 (s, 3 H, CC*Me*)	
8	2.11 (s, 30 H)	7.01 (t, 1 H, J = 6.0, *p*-H), 7.14 (t, 2 H, J = 6.0, *m*-H), 7.69 (d, 2 H, *o*-H)	0.91 (t, 6 H, J = 7.03, β-Et), 3.40 (q, 4 H, α-Et)
9	2.06 (s, 30 H)	0.34 (s, 9 H, SiMe_3)	0.91 (t, 6 H, J = 7.03, β-Et), 3.32 (q, 4 H, α-Et)
10		1.84 (s, 3 H, C=C*Me*), 1.94 (s, 3 H, C=C*Me*), 5.14 (d, 1 H, ^2J = 1.83, (*Z*)-C*H*), 5.17 (d, 1 H, (*E*)-C*H*)	
13	1.84 (s, 30 H)	6.62 (ddd, 1 H, J_{bc} = 7.03, J_{cd} = 7.26, J_{ac} = 1.50, H_c), 7.10 (ddd, 1 H, J_{ab} = 7.32, J_{bd} = 1.50, H_b), 7.78 (dd, 1 H, H_a), 7.99 (dd, 1 H, H_d)	
14	1.84 (s, 30 H)	6.64 (ddd, 1 H, J_{bc} = 7.32, J_{cd} = 7.31, J_{ac} = 1.47, H_c), 7.11 (ddd, 1 H, J_{ab} = 7.31, J_{bd} = 1.48, H_b), 7.75 (ddd, 1 H, J_{YH} = 2.64, H_a), 8.08 (ddd, 1 H, J_{YH} = 2.05, H_d)	1.36 (m, 4 H, β-THF), 3.44 (m, 4 H, α-THF)
15	1.86 (s, 30 H)	2.21 (s, 3 H, α-Me), 6.52 (d, 1 H, J_{bc} = 7.62, H_c), 7.04 (dd, 1 H, J_{ab} = 7.62, H_b), 7.65 (d, 1 H, H_a)	1.36 (m, 4 H, β-THF) 3.57 (m, 4 H, α-THF)
16	1.84 (s, 30 H)	1.97 (d, 2 H, $^2J_{YH}$ = 3.70, YC*H*$_2$), 2.10 (s, 6 H, 3,5-*Me*), 6.13 (s, 2 H, *o*-H), 6.31 (s, 1 H, *p*-H)	
17	1.93 (s, 30 H)	1.67 (d, 2 H, $^2J_{YH}$ = 3.55, YC*H*$_2$), 2.45 (s, 6 H, 3,5-*Me*), 6.37 (s, 1 H, *p*-H), 6.64 (s, 2 H, *o*-H)	1.25 (m, 4 H, β-THF) 3.28 (m, 4 H, α-THF)
18a[b]	2.12 (s, 30 H)	2.68 (dd, 1 H, $^1J_{YH}$ = 68.08, $^1J_{YH}$ = 32.12, Y-H-Y)	
19a	2.08 (s, 30 H)	6.17 (d, 1 H, $^1J_{YH}$ = 81.74, Y-H)	

[a] 90-MHz spectra in C_6D_6 at 20 °C; δ in ppm; δ(Me_4Si) 0.0; J is $^3J_{HH}$ in Hz unless stated otherwise. [b] In C_6D_{12} at 20 °C.

(m). The product **10** was separated from the toluene by distillation, bp 82 °C (lit. 81–82 °C). IR (KBr, neat, cm^{-1}): 3070 (w), 2950 (m), 2900 (s), 2840 (m), 2720 (w), 2210 (m), 1605 (s), 1430 (m), 1360 (m), 1280 (m), 1000 (w), 885 (s), 630 (w), 540 (w), 510 (w), 455 (w).

2,4-Diphenyl-1-buten-3-yne (11). To a solution of 22 mg of **1** (0.04 mmol) in 10 mL of toluene was added 2.0 mL of phenylethyne (18.0 mmol). The mixture was stirred for 2 h at room temperature, and reaction was quenched with 2 mL of a 0.1 M HCl solution. The solvent was pumped off and the residue washed with water and dried. Isolated yield: 1.63 g of **11** (16.0 mmol, 89%) as a colorless solid. The IR and ^{1}H NMR spectra are identical with those reported by Akita et al.[10]

2,4-Bis(trimethylsilyl)-1-buten-3-yne (12). Starting with 1.24 mL of HC≡CSiMe_3 (9.05 mmol) **12** was prepared as described above. The colorless liquid was distilled and identified by IR and ^{1}H NMR spectra.[10] Yield: 1.53 g of **12** (7.78 mmol, 86%).

Cp*$_2$Y(η^2-NC$_5$H$_4$) (13). A NMR tube charged with 41.3 mg of **1** (0.08 mmol), 6.4 μL of pyridine (0.08 mmol), and 0.35 mL of C_6D_6 was sealed, and the ^{1}H NMR spectrum was monitored at regular intervals for 3 days. The spectra recorded after 3 h showed the resonances of **13** and $CH_2(SiMe_3)_2$ as well as the pyridine adduct of **1**. The reaction was completed after ca. 48 h. A preparative experiment gave **13** as a red oil. IR (cm^{-1}): 3040 (w), 2720 (w), 1595 (s), 1580 (m), 1480 (m), 1365 (m), 1335 (m), 1245 (s), 1210 (m), 1145 (w), 1070 (m), 1030 (m), 950 (w), 865 (s), 800 (w), 750 (m), 700 (s), 615 (m), 590 (w), 530 (w), 405 (m).

Cp*$_2$Y(η^2-NC$_5$H$_4$)·THF (14). A mixture of 25.7 mg of **2** (0.06 mmol) and 4.6 μL of pyridine (0.06 mmol) in 0.4 mL of C_6D_6 was studied by ^{1}H NMR in a sealed NMR tube. After 15 min the resonances of the starting materials had disappeared completely. The new signals present were assigned to **14** (Table I) and CH_4 (δ 0.16).

Cp*$_2$Y(η^2-NC$_5$H$_3$-6-Me)·THF (15). The ^{1}H NMR spectrum of a mixture of 16.2 mg of **2** (0.04 mmol) and 3.6 μL of α-picoline (0.04 mmol) in 0.35 mL of C_6D_6 was recorded. The resonances of the starting materials were not observed, and the spectrum showed the signals of **15** (Table I) and CH_4.

Cp*$_2$YDMB (16). A solution of 5.37 g of **1** (10.36 mmol) in 60 mL of mesitylene was stirred at 150 °C for 24 h. The solvent was removed at reduced pressure, and the remaining orange solid was extracted with pentane. The clear yellow solution was concentrated until crystallization started and stored at −30 °C. The yellow crystals formed were filtered off to give 2.55 g of **16**. Concentrating the mother liquor afforded a second crop. Overall yield: 4.07 g of **16** (8.50 mmol, 82%). IR (cm^{-1}): 3020 (m), 2720 (w), 1590 (s), 1560 (s), 1485 (m), 1390 (w), 1365 (m), 1310 (m), 1285 (m), 1160 (s), 1065 (w), 1020 (m), 980 (w), 925 (w), 875 (m), 840 (s), 820 (s), 800 (w), 770 (w), 700 (m), 685 (w), 660 (w), 610 (w), 595 (w), 580 (w), 525 (m), 505 (s), 470 (w), 375 (m). Anal. Calcd for $C_{29}H_{41}Y$: C, 72.79; H, 8.64. Found: C, 72.80; H, 8.64.

Cp*$_2$YDMB·THF (17). To a solution of 0.74 g of **16** (1.55 mmol) in 30 mL of pentane was added 0.2 mL of THF (2.46 mmol) at room temperature, and the mixture was stirred for 2 h. After filtration the clear solution was stored at −80 °C to give 0.31 g of **17** (0.57 mmol, 36%) as colorless crystals. IR (cm^{-1}): 3020 (m), 2720 (w), 1580 (m), 1485 (m), 1365 (m), 1295 (m), 1240 (w), 1200 (w), 1155 (m), 1040 (w), 1020 (m), 1010 (s), 905 (s), 860 (m), 845 (m), 815 (m), 800 (w), 690 (m), 655 (m), 595 (w), 550 (m), 520 (w), 420 (w). Anal. Calcd for $C_{35}H_{49}YO$: C, 71.98; H, 8.97. Found: C, 71.72; H, 8.93.

(Cp*$_2$YH)$_2$ (18a). A solution of 0.63 g of **1** (1.27 mmol) in 20 mL of pentane was stirred under H_2 (p = 760 mmHg) for 6 h at 0 °C. The solution turned reddish, and a white solid deposited. The solution was decanted and the white solid isolated. Yield: 0.33 g of **18a** (0.93 mmol, 78%). IR (cm^{-1}): 2720 (w), 1495 (m), 1365 (m), 1272 (m, br) [ν_{YH}], 1060 (w) , 1020 (m), 805 (w), 655 (m) [ν_{YH}], 590 (m), 415 (m). Anal. Calcd for $C_{20}H_{31}Y$: C, 66.66; H, 8.67. Found: C, 66,59; H, 8.72.

(Cp*$_2$YD)$_2$ (18b). The deuteride **18b** was synthesized similar to **18a**. IR (cm^{-1}): 2720 (w), 1495 (m), 1365 (m), 1245 (w), 1060 (w), 1020 (m), 920 (m, br) [ν_{YD}], 800 (w), 590 (w), 465 (m) [ν_{YD}], 425 (m). ν_{YH}/ν_{YD}: calcd 1.41, found 1.38 and 1.41.

Cp*$_2$YH·THF (19a). A solution of 0.21 g of **18a** (0.58 mmol) in 10 mL of benzene was stirred at room temperature for 2 h with 0.11 mL of THF (1.35 mmol). The solvent was removed completely by evaporation and the white solid washed with 10 mL of cold pentane (−20 °C) and isolated. Yield: 0.07 g of **19a** (0.16 mmol, 28%). IR (cm^{-1}): 2720 (w), 1490 (m), 1365 (m), 1295 (s, br) [ν_{YH}], 1240 (m), 1140 (s), 1100 (m), 1060 (m), 1020 (s), 950 (w), 920 (m), 870 (s), 845 (m), 805 (w), 725 (m), 670 (m), 630 (s), 600 (w), 550 (m). Anal. Calcd for $C_{24}H_{39}YO$: C, 66.65; H, 9.09. Found: C, 66.40; H, 8.95.

Cp*$_2$YD·THF (19b). Complex **19b** was prepared similar to **19a**. IR (cm^{-1}): 2720 (w), 1490 (m), 1365 (m), 1245 (m), 1140 (s), 1095 (m), 1060 (w), 1020 (s), 950 (w), 920 (m, br) [ν_{YD} and THF], 870 (s), 845 (m), 800 (w), 660 (s), 630 (m), 595 (w), 550 (w). ν_{YH}/ν_{YD}: calcd 1.41, found 1.41.

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Table II. $^{13}C\{^1H\}$ NMR Data[a] of the New Cp^*_2Y Compounds

complex	C_5Me_5	C_5Me_5	R/L
3	10.57 (q, 125.3)	116.90 (s)	28.02 (q, 126.7, O=C*Me*), 101.68 (d, 157.0, C*CH*C), 191.00 (d, $^2J_{YC}$ = 2.5, O=*C*)
5	11.50 (q, 124.9)	116.35 (s)	14.45 (q, 125.9, β-OEt_2), 22.25 (q, 124.5, β-OEt), 61.74 (t, 141.3, α-OEt), 66.54 (t, 140.1, α-OEt_2)
6	11.61 (q, 125.1)	116.63 (s)	14.54 (q, 126.4, β-OEt_2), 28.81 (q, 124.0, OCH*Me*$_2$), 66.11 (t, 143.8, α-OEt_2), 67.03 (dd, 140.8, $^2J_{YC}$ = 4.1, YOCH)
7a	12.02 (q, 125.1)	117.39 (s)	5.85 (q, 128.1, C≡C*Me*), 14.24 (q, 126.3, β-OEt_2), 66.25 (t, 144.4, α-OEt_2), 102.32 (d, $^2J_{YC}$ = 10.8, YC≡*C*), 133.04 (d, $^1J_{YC}$ = 73.9, Y*C*≡C)
8	12.02 (q, 125.1)	117.70 (s)	14.37 (q, 125.4, β-OEt_2), 66.27 (t, 144.0, α-OEt_2), 109.59 (d, $^2J_{YC}$ = 12.9, YC≡*C*), 125.50 (d, 157.9, *p*-C(Ph)), 126.47 (s, α-C(Ph)), 128.25 (s, 169.3, *o*-C(Ph)), 131.56 (d, 165.2, *m*-C(Ph)), 146.95 (d, $^1J_{YC}$ = 70.9, Y*C*≡C)
9	12.06 (q, 124.8)	117.67 (s)	1.37 (q, 118.5, $SiMe_3$), 14.49 (q, 125.5, β-OEt_2), 66.21 (t, 143.9, α-OEt_2), 114.19 (d, $^2J_{YC}$ = 6.1, YC≡*C*), 134.21 (d, $^1J_{YC}$ = 72.0, Y*C*≡C)
16[b]	11.77 (q, 125.3)	118.75 (s)	22.64 (q, 125.7, 3,5-*Me*), 47.35 (dt, 133.4, $^1J_{YC}$ = 23.2, Y*C*), 116.16 (d, 142.1, *o*-C), 123.62 (d, 155.2, *p*-C), 142.70 (s, *m*-C), 156.26 (s, α-C)
17	11.64 (q, 125.1)	117.25 (s)	21.84 (q, 125.2, 3,5-*Me*), 25.24 (t, 133.5, β-THF), 46.43 (dt, 117.4, $^1J_{YC}$ = 39.6, YC), 70.40 (t, 148.7, α-THF), 119.93 (d, 159.5, *p*-C), 122.13 (d, 150.3, *o*-C), 137.32 (s, *m*-C), 155.85 (s, α-C)

[a] 50.3-MHz spectra in C_6D_6 at 20 °C; δ in ppm; δ(Me_4Si) 0.0. Between parentheses multiplicity, coupling constants ($^1J_{CH}$) in Hz, and resonance assignment. [b] In C_6D_{12} at 20 °C.

H/D Exchange Experiments. The H/D scrambling was monitored by ^1H NMR. Solutions for these experiments were prepared in the glovebox and sealed in NMR tubes. The concentration of the yttrium complexes involved was about 0.15–0.20 M. The ^1H NMR spectra were recorded at intervals of 2 h.

Results and Discussion

General Considerations. One common aspect of the reactions of the monomeric permethylyttrocene complexes $Cp^*_2YCH(SiMe_3)_2$ (1) and $Cp^*_2YMe\cdot THF$ (2) described here is that only the YC bond seems to be affected, leading to a variety of new Cp^*_2Y derivatives. As far as can be concluded from the products isolated and the spectroscopic studies (NMR (Tables I and II) and IR) the cyclopentadienyl ligands are not actively involved[11] and the bent permethylyttrocene structure remains intact in all cases.

With respect to the substrate molecules the reactions can be classified as hydrogen transfer from the substrate to the carbon atom of the alkyl group originally bonded to yttrium.

Specific Reactions. With regular H^+ reagents like HCl, 1 and 2 give, not surprisingly, the chlorides $(Cp^*_2YCl)_2$[9a] and $Cp^*_2YCl\cdot THF$.[3,9b] The reaction of 1 with acetylacetone gives $Cp^*_2Y(acac)$ (3) (eq 1). The acetylacetonate ligand in 3 is undoubtedly bonded in an η^2 fashion (IR[12]).

$$\underset{1}{Cp^*_2YCH(SiMe_3)_2} + MeCOCH_2COMe \xrightarrow[20\ °C]{Et_2O} \underset{3}{Cp^*_2Yacac} + CH_2(SiMe_3)_2 \quad (1)$$

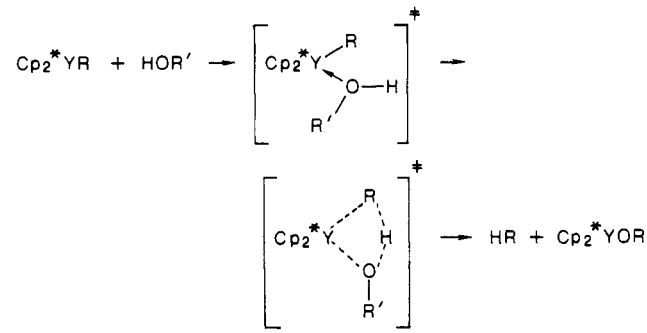
Yttrocene alkoxides, $Cp^*_2YOR\cdot L$, can be obtained from 1 and the appropriate alcohols (eq 2). With ether as a

$$\underset{1}{Cp^*_2YCH(SiMe_3)_2} + ROH \xrightarrow[20\ °C]{Et_2O} Cp^*_2YOR\cdot OEt + CH_2(SiMe_3)_2 \quad (2)$$

4, R = Me
5, R = Et
6, R = *i*-Pr

solvent one molecule of Et_2O remains coordinated to yttrium, illustrating the distinct Lewis acidity of the metal center in Cp^*_2Y derivatives.[4,8] The driving force in these reactions seems to be formation of an yttrium–oxygen bond (D^0_{298} = 170.9 ± 3.0 kcal/mol[13]), which is far stronger than an yttrium–carbon bond (D^0_{298} = 100 ± 15 kcal/mol[13]).

Scheme I



With respect to the mechanism of these reactions two pathways can be considered. The most likely—at first sight—is straightforward protolysis. The reactions then should be fast, and the rate would depend on the acid strength of the substrate. Those with smaller pK_a values would give faster reactions, and the order MeOH ≃ EtOH < *i*-Pr < *t*-BuOH is expected then.[14] The observations, however, are exactly opposite. The reactions with MeOH and EtOH are rather fast and go on to completion within 1 h. The alcoholysis with *i*-PrOH proceeds much slower (completion after 26 h), and with *t*-BuOH no reaction is observed at all (48 h, 25 °C). A mechanism that accounts for this is the "σ-bond metathesis" (Scheme I) as presented by Watson[8] and others,[1b,15] to explain C–H activation and hydrogenolysis reactions on related groups and 4f elements.

In this mechanism precomplexation of the alcohol is essential in order to achieve the "four-centered" transition state and steric effects on both the alkyl group on the alcohol and yttrium are expected to determine the reaction rate. Inspection of the structure of 1[3] shows that sufficient space is available for complexation of small alcohols. A bulky alcohol like *t*-BuOH does not fit in, which explains its lack of reactivity.

Mechanisms of this type appear to be more general in this area of chemistry and also intermolecular CH activations may follow this route. Recent review articles on

(11) In contrast with the yttrium chemistry reported here the involvement of the Cp* ligands is in Cp^*_2TiR chemistry of crucial importance: Luinstra, G. A.; Pattiasina, J. W.; Teuben, J. H., manuscript in preparation.

(12) The IR spectrum shows the bidentate acac vibrations at 1580 (s), 1515 (s), and 1390 (s) cm^{-1}: cf. Couts, R. S. P.; Wailes, P. C. *J. Organomet. Chem.* **1970**, *25*, 117.

(13) Weast, R. C. *CRC Handbook of Chemistry and Physics*, 60th ed.; RCR Press: Boca Raton, FL 1975; p F220.

(14) Brauman, J. L.; Blair, L. K. *J. Am. Chem. Soc.* **1970**, *92*, 5986.

(15) (a) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, N. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111.

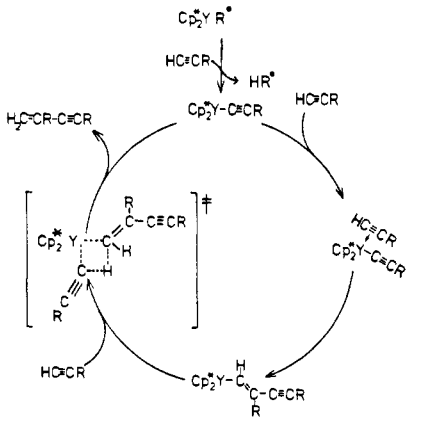


Figure 1. Catalytic cycle for α-alkyne dimerization.

this topic[16,17] do take this mechanism into account, and recent quantum chemical calculations[18] have demonstrated that this reaction pathway is allowed in d^0 metallocenes.

In our work the metalation of α-alkynes (eq 3) can be explained satisfactorily with this mechanism. The methyl

$$\underset{\mathbf{1}}{Cp^*_2YCH(SiMe_3)_2} + HC{\equiv}CR \xrightarrow[20\ °C]{Et_2O} Cp^*_2YC{\equiv}CR{\cdot}OEt + CH_2(SiMe_3)_2 \quad (3)$$

7a, R = Me
8, R = Ph
9, R = $SiMe_3$

complex **2** reacts in a similar way; e.g., propyne gives $Cp^*_2YC{\equiv}CMe{\cdot}THF$ (**7b**). The alkynyl ligands are rodlike and leave sufficient space around the metal center to admit relief of the coordinative unsaturation by formation of 16-electron adducts $Cp^*_2YC{\equiv}CR{\cdot}L$ (L = OEt_2 or THF). These adducts are quite stable and show no further reactivity toward acetylenes. A complete different picture is obtained in the absence of ether bases. Reaction of **1** with propyne in a noncoordinating solvent resulted in the formation of 2-methyl-1-penten-3-yne (**10**), while the bulk of the yttrium compound **1** was recovered. Apparently this reaction is catalytic as was confirmed by further experiments. Complex **1** is very active in the dimerization of a variety of α-alkynes (eq 4). The turnover number in the

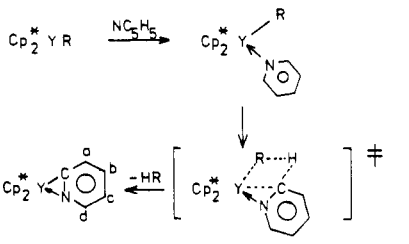
$$2HC{\equiv}CR \xrightarrow[\text{toluene}]{[1]} H_2C{=}C(R)C{\equiv}CR \quad (4)$$

10, R = Me
11, R = Ph
12, R = $SiMe_3$

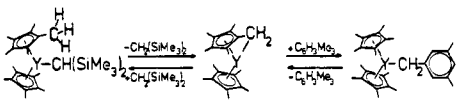
propyne reaction is 5400 h^{-1} at 20 °C and 1 atm of propyne. The methyl complex is totally inreactive with respect to this dimerization. A plausible cycle for the dimerization is given in Figure 1. The essential step is the insertion of a carbon–carbon triple bond in the sp-carbon–yttrium bond, where the steric bulk of the group R probably causes the regioselectivity of the dimerization. Similar dimerizations have been reported in permethyltitanocene[10] and organopalladium[19] chemistry, and currently we are exploring the scope of this reaction in the yttrium system.

The permethylyttrocenes **1** and **2** metalate pyridines to the *o*-pyridyl complexes. Starting from **1** and pyridine the 16-electron compound $Cp^*_2Y(\eta^2\text{-}NC_5H_4)$ (**13**) is obtained, but ortho-substituted pyridines like α-picoline do not seem

Scheme II



Scheme III



to react. Compound **2** shows basically the same reaction and also metalates α-picoline easily. The THF ligand appears not to interfere the metalation reaction. Presumably it is dissociated from **2** to give the pyridine adduct, which then metalates under extrusion of methane. After the reaction the THF molecule coordinates again to the metal center under formation of the 18-electron systems $Cp^*_2Y(\eta^2\text{-}NC_5H_4){\cdot}THF$ (**14**) and $Cp^*_2Y(\eta^2\text{-}NC_5H_3\text{-}6\text{-}Me){\cdot}THF$ (**15**). This metalation of pyridines seems a typical reaction for early transition metals (Sc,[15a] Ti[6]) and 4f-element (Lu[20]) σ-carbon bonds in derivatives Cp^*_2MR or Cp_2MR.

Discussions on the mechanism of these reactions all assume precomplexation of the pyridine ligand to the metal center prior to hydrogen transfer from the pyridine to the alkyl group via a $[2_s + 2_s]$ transition state (Scheme II). For yttrium a related pyridine adduct has been reported.[21] The complexation step is essential, and if sterically hindered by large substituents on the metal center or when the coordination site is occupied by a firmly bonded ligand, the metallation may be slowed down dramatically or even not occur at all. The latter is observed when **1** is reacted with α-picoline. In the reactions of **2** with pyridines the THF ligand seems to be exchanged rapidly and the metalation is so fast that a pyridine adduct cannot be observed. For the compound **1** the large ligand $CH(SiMe_3)_2$ slows down the reaction considerably and the transient adduct $Cp^*_2YCH(SiMe_3)_2{\cdot}NC_5H_5$ can be identified by ^1H NMR.[22]

It is not absolutely necessary to have a ligating atom close to the "active" CH bond to force this bond into the proximity of the YC bond so that metalation can follow. This is illustrated in the metalation reaction of mesitylene by **1** (eq 5). The reaction is surprisingly selective and a

$$\underset{\mathbf{1}}{Cp^*_2YCH(SiMe_3)_2} \xrightarrow[150\ °C]{\text{mesitylene}} Cp^*_2YDMB + CH_2(SiMe_3)_2 \quad (5)$$

16

very efficient route for the synthesis of the salt-free, monomeric, permethylyttrocene benzyl Cp^*_2YDMB (**16**). This fascinating reaction rises the question whether other sp^3-CH bonds can be activated also. We anticipated reaction of **1** with toluene at 100 °C and found a mixture of benzyl, *o*-, *m*-, and *p*-tolylyttrocenes (^1H NMR). Thus,

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(21) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291.
(22) 90-MHz ^1H NMR of $Cp^*_2YCH(SiMe_3)_2{\cdot}NC_5H_5$ (C_6D_6, 20 °C, δ-(Me_4Si) 0.0): δ −0.07 (d, 1 H, $^2J_{YH}$ = 3.5 Hz, YCH), 0.20 (s, 18 H, $SiMe_3$), 1.84 (s, 15 H, C_5Me_5), 1.91 (s, 15 H, C_5Me_5), 6.55 (m, 2 H, $o\text{-}H_{pyr}$), 6.87 (m, 1 H, $p\text{-}H_{pyr}$), 8.29 (m, 2 H, $m\text{-}H_{pyr}$).

with toluene the metalation is not restricted to the sp^3-CH bond. In the reaction with mesitylene the sp^2-CH bonds appear not to be activated. A plausible explanation for this may be that the methyl groups in mesitylene block the necessary transition state for metalation of the aromatic nucleus. Methane appeared not to react with **1** up to 100 °C in C_6D_{12} (4 atm of CH_4, 14 days) as **1** was isolated unchanged.

With respect to the mechanism of the metalation of mesitylene a $[2_s + 2_s]$ reaction pathway like assumed for the before-mentioned reactions seems the most attractive. An alternative route (Scheme III), however, cannot be excluded a priori as the reaction proceeds at 150 °C. At this temperature the thermolysis of **1** starts to take place and hydrogen abstraction from a methyl group of a Cp* ligand to give a Fv* derivative may occur. Against this second route is that in the only well-defined Fv*-containing yttrium complex $Cp^*_2Y(\mu\text{-}H)(\mu\text{-}Fv^*)YCp^*$,[23] the Y–$CH_2$ moiety has no tendency to activate CH or CD bonds. So, for the time being, we favor the direct σ-bond metathesis mechanism.

The coordinative unsaturation of **16** can be lowered by complexation of a THF molecule giving Cp^*_2YDMB·THF (**17**). Noteworthy is that in both **16** and **17** the bonding of the benzylic ligand appears to be η^1. Allylic η^3-coordination as might have been expected in **16** on the basis of the coordinative unsaturation does not take place.

Besides the activation of XH bonds by a metal center as discussed above, the σ-bond metathesis mechanism also provides a plausible reaction pathway for the hydrogenolysis of the YC bond in both **1** and **2** in nonpolar solvents. The reaction products are $(Cp^*_2YH)_2$ (**18a**) and Cp^*_2YH·THF (**19a**), respectively. If hydrogenolysis is a metathetical reaction, then a competing reagent, which can block the coordination of the H_2 molecule, would slow down or prevent this reaction. Indeed when these reactions were attempted in THF or Et_2O, the carbyls **1** and **2** did not react and were recovered quantitatively. This parallels the observations reported by Evans et al.[24] on hydrogenolysis studies of 4f-metallocene carbyls. These authors argue that coordinatively unsaturated metal centers are an absolute necessity for the reaction. Apparently, in nonpolar solvents, for **2** some dissociation of the THF ligand occurs to provide access to the highly reactive, unsaturated species.

The hydride **18a** is easily converted to **19a** (eq 6).

$$\underset{\textbf{18a}}{(Cp^*_2YH)_2} + 2THF \rightarrow 2\underset{\textbf{19a}}{Cp^*_2YH\cdot THF} \qquad (6)$$

The XH-activation reactions described above all give new permethylyttrocene complexes, which are not easily prepared by other, more conventional routes.

H/D Scrambling between sp^2-CD and sp^3-CH Bonds. Very interesting H/D scrambling was observed with the hydride **18a**. In C_6D_6 at room temperature the hydride ligand is exchanged for deuterium very rapidly and quantitatively. The deuteride $(Cp^*_2YD)_2$ (**18b**) can be synthesized conveniently this way. Yttrium behaves in this respect very similar to lutetium.[20] In the presence of $CH_2(SiMe_3)_2$ the hydride **18** catalyzes the H/D exchange between the methyl groups of the trimethylsilyl fragments and C_6D_6 and the methylene group is not affected (Figure 2). The half-life time of this scrambling reaction (50% deuteriation) at room temperature was 27 h. Since the methyl group of toluene is also deuteriated by **18** in C_6D_6, apparently in a similar reaction, it seems that this hydride is an effective catalyst for the deuteriation of methyl groups. In the latter system also the phenyl group is affected but at a much lower rate, showing the preference for sp^3-CH bonds.

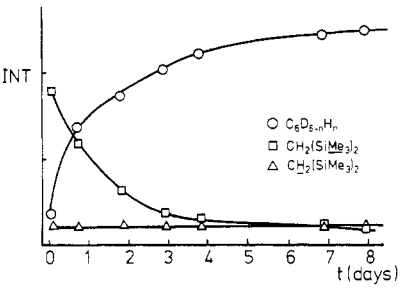

Figure 2. H/D exchange between $CH_2(SiMe_3)_2$ and C_6D_6 (intensity of the ^1H NMR signals vs. time).

The fact that the Cp* ligands are not involved in these scrambling processes makes routes, via Fv*Y intermediates, very unlikely. These intermediates, however, seem to play an important role in the H/D scrambling at higher temperatures and with other elements, e.g., Sc[15a] and Ti.[11] The deuteriation of $SiMe_3$ groups at 100 °C shows that, in addition to the expected rate increase, also the Cp* ligands are deuteriated completely within 4 h. In order to explain this Fv* intermediates must have been involved. Although the isolation of $Cp^*_2Y(\mu\text{-}H)(\mu\text{-}Fv^*)YCp^*$[23] strongly suggests an intermolecular pathway, the mechanism of the Cp* deuteriation remains obscure.

Spectroscopic Characterization. All new complexes have been fully characterized by NMR (Tables I and II), IR, and elemental analyses. The spectra show that all complexes have the bent metallocene structure[3,4] together with the usual characteristics of the other ligands. A detailed discussion of all spectroscopic data seems not appropriate here; however, some outstanding features will be emphasized below.

An extremely important tool in the interpretation of NMR spectra is the nuclear spin momentum of yttrium ($I = {}^1/_2$, monoisotopic[25]), since first- and second-order couplings with the nuclei bonded to yttrium are observed. Thus, interpretation of the spectra, especially the identification of the atoms bonded directly to yttrium, is considerably facilitated as is demonstrated in the following three examples.

The ^{13}C NMR spectra of the complexes **7a**, **8**, and **9** show yttrium carbon coupling on the α- and β-carbon atoms of the alkynyl ligands. The magnitude of the couplings ($J_{Y,C}$) enables us to discriminate between the α- and β-carbons. The resonances with the largest coupling constants are assigned to the α-carbons. The couplings ($^1J_{YC}$) on the α-carbon signals are 73.9 Hz (δ 133.04) in **7a**, 70.9 Hz (δ 146.95) in **8**, and 72.0 Hz (δ 134.21) in **9**. The resonances are doublets, and this observation justifies the conclusion that the complexes are monomeric in solution. In the case of bridging alkynyl groups either a triplet (symmetric bridge) or a double doublet (asymmetric bridge) signal would have been observed. The coupling constants are much larger than those reported so far for the permethylyttrocene alkyls (**1**, $^1J_{YC}$ = 36.6 Hz; **2**, $^1J_{YC}$ = 56.2 Hz; $(Cp^*_2YMe)_2$, $^1J_{YC}$ = 42.7 and 51.1 Hz). The larger coupling constants in the alkynyl complexes can be explained by increased σ-character of the metal–carbon bond,

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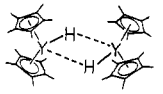

Figure 3. Proposed structure of $(Cp^*_2YH)_2$.

caused by the larger s character of a sp-carbon orbital.[26] The seond-order yttrium coupling on the β-alkynyl carbon is far smaller. The $^2J_{YC}$ values are 10.8 Hz (δ 102.32) in **7a**, 12.9 Hz (δ 109.59) in **8**, and 6.1 Hz (δ 114.19) in **9**. Thus, in addition to a reliable assignment of the resonances the coupling constants also provide information on the state of aggregation of the molecules in solution.

The second example is formed by the hydrides **18** and **19**. The ^{1}H NMR spectrum of **18a** shows one hydride resonance (δ 2.86) as a double doublet ($^1J_{YH}$ = 68.08 and 32.12 Hz). This means that the hydride experiences two inequivalent interactions with two yttrium nuclei. An asymmetric dimeric hydride (Figure 3) is the most probable structure for **18**. In the case of symmetric hydride bridges a triplet signal would be expected.[27] The largest coupling constant is assigned to the more or less regular YH bond, as it expresses a stronger interaction between the nuclei. The possibility of a dimer with one terminal and one bridging hydride ligand, cf. $(Cp^*_2YMe)_2$[8] and $(Cp^*_2YCl)_2$,[9] can be excluded on the basis of the observation of only one hydride resonance with correct intensity. The hydride THF adduct **19a** has a doublet hydride signal in the ^{1}H NMR at δ 6.17 ($^1J_{YH}$ = 81.74 Hz). Thus, the complex **19** is monomeric in solution.

The final example in which the yttrium coupling reveals extra information with respect to the bonding in yttrocene compounds, deals with the coordination of the benzyl ligand in **16** and **17**. IR spectra indicate that in both complexes the DMB ligand is σ-bonded to the metal center. Characteristic absorptions for a σ-benzyl[28] are observed, at 1590 and 1560 cm^{-1} in **16** and at 1580 cm^{-1} in **17**, while for π-bonded benzyl ligands a weak absorption at about 1530 cm^{-1} is expected.[28]

In the ^{13}C{^{1}H} NMR spectrum of **17** (Table II) the methylene resonance is observed (δ 46.43) as a double triplet ($^1J_{YC}$ = 39.6; $^1J_{CH}$ = 117.4 Hz). The values of $^1J_{YC}$ and $^1J_{CH}$ are normal for σ-YC (vide supra) and sp^3-CH bonds.[26] Also the position (δ 122.13) and coupling constant ($^1J_{CH}$ = 150.3 Hz) of the ortho-carbon atoms of the phenyl ring of the DMB ligand are as expected for a normal sp^2-CH bond.[26] The ^{1}H NMR spectrum is consistent with a σ-bonded benzylic ligand (Table I, methylene protons δ 1.67 ($^2J_{YH}$ = 3.55 Hz); ortho protons δ 6.64 ppm). In conclusion, spectroscopic evidence indicates that in **17** the DMB ligand is regularly σ-bonded to yttrium.

In complex **16** the bonding of the DMB ligand is essentially different. The ^{1}H NMR of **16** at 20 °C gives a doublet at δ 1.97 ($^2J_{YH}$ = 3.70 Hz) for the methylene group, and the ortho hydrogens of the phenyl ring resonate at δ 6.13. The ^{13}C{^{1}H} NMR spectrum shows the methylene carbon at δ 47.35 as a double triplet ($^1J_{YC}$ = 23.2, $^1J_{CH}$ = 133.4 Hz) and the ortho-carbon signal at δ 116.16 as a doublet ($^1J_{CH}$ = 142.1 Hz). Compared with **17** the signals of the ortho-CH moiety of the phenyl ring are shifted to higher field and the coupling constant $^1J_{CH}$ has decreased. For the methylene group the ^{13}C resonances are almost at the same position (**16**, δ 47.35, vs. **18**, δ 46.43). The coupling

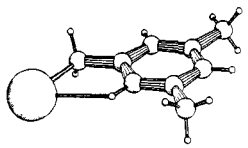

Figure 4. γ-Agostic interaction in Cp^*_2YDMB.

constants $^1J_{YC}$ and $^1J_{CH}$, however, have changed dramatically; the yttrium coupling increases (**16**, 23.2 Hz, **17**, 39.6 Hz) whereas the CH coupling decreases (**16**, 133.4 Hz, **17**, 117.4 Hz). A possible explanation could be that the benzyl ligand in **16** is π-bonded to yttrium. Arguments against η^3-coordination of the DMB ligand in **16**, besides the IR spectrum, are found in the details of the NMR data of the benzylic CH_2 group. These methylene protons are equivalent. In the cases of π-bonding two resonances are expected for the endo and the exo protons. Furthermore, if YC coupling still can be observed on the methylene carbon, when the DMB ligand is allylic, it is also expected on the ortho-carbon resonance, which should then be a doublet. These features are not observed, and thus the changes in chemical shifts and coupling constants must have another origin.

An indication of what is actually happening may be found in the $^1J_{CH}$ on the ortho-carbon signal in the ^{13}C{^{1}H} NMR, which is too small for a regular sp^2-CH bond.[26] It suggests a lowering of the s character of the CH bond. A plausible cause of such a lowering could be the presence of an interaction of the electron-deficient metal center with the electron density of the CH bond. This leads then to a "γ-agostic Y···CH bond"[29] (Figure 4). In complex **17** both ortho-CH bonds can give this interaction, and when this is a "fluxional γ-agostic interaction", it will lead to equivalent NMR features for the two ortho-CH fragments.

The possibility of freezing out a dynamic agostic behavior at low temperatures has been pointed out by Brookhart and Green.[29] In our case we would expect at low temperatures a two-electron, three-centered σ-CH···Y system, in which yttrium coupling on the C and H nuclei of the agostic CH fragment could be present. The ^{1}H and proton-decoupled ^{13}C NMR spectra of **16** at −80 °C[30] indeed show the expected features, which provide the solution to the problem of the bonding of the DMB ligand in **16**. The methylene group still shows one doublet resonance, in both spectra, and the single Cp* resonances show that these ligands are still equivalent. Thus, also at −80 °C the DMB ligand is not coordinated as an η^3-allylic ligand. The other signals demonstrate that the benzylic ligand is bonded asymmetrically to yttrium. In the ^{13}C NMR spectrum there are six ring carbon resonances and two methyl carbon signals. The ^{1}H NMR spectrum also shows two methyl groups, and the three ring protons are observed with equal intensities.

An outstanding aspect is that at −80 °C one of the ortho-CH bonds interacts with yttrium giving doublet signals due to yttrium coupling, in both ^{1}H and ^{13}C NMR spectra. The $^1J_{YH}$ (32.84 Hz) almost equals the coupling of the YH bridge in the hydride **18a** ($^1J_{YH}$ = 32.12 Hz) and the $^1J_{YC}$ (22.2 Hz) on the ortho-carbon signal is comparable the yttrium coupling on the methylene carbon resonance ($^1J_{YC}$

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(30) ^{1}H and ^{13}C NMR spectra of **16** at −80 °C in toluene-d_8 (δ-(Me_4Si)0.0). ^{1}H NMR: δ 1.76 (s, 30 H, C_5Me_5), 1.93 and 1.96 (s, 3 H, 3,5-Me), 2.04 (d, 2 H, $^2J_{YH}$ = 4.01 Hz, YCH_2), 6.18 (s, 1 H, *p*-H), 6.23 (s, 1 H, *o*-H), 6.93 (d, 1 H, $^1J_{YH}$ = 32.84 Hz, *o*-H···Y). ^{13}C NMR: δ 11.01 (s, C_5Me_5), 21.36 (s, Me_{DMB}), 21.75 (s, Me_{DMB}), 47.48 (d, $^1J_{YC}$ = 20.3 Hz, YCH_2), 113.98 (s, *p*-C), 117.35 (s, C_5Me_5), 120.03 (d, $^1J_{YC}$ = 22.2 Hz, *o*-C···Y), 124.37 (s, *o*-C), 141.43 (s, *m*-C), 142.02 (s, *m*-C), 154.91 (s, α-C).

= 20.3 Hz) at this temperature. These couplings show that the γ-agostic interaction has σ-symmetry, with respect to the metal center. Otherwise no yttrium coupling on the interacting CH fragment would have been observed.

The spectroscopy of **16** clearly indicates the presence of a γ-agostic interaction in this complex between the Lewis acid yttrium and one of the ortho-CH bonds of the DMB ligand. This interaction is static at −80 °C, while at higher temperatures both ortho-CH bonds are involved due to dynamic processes like rotation and wagging.[3] Moreover, the NMR study of **16** demonstrates the potential of NMR spectroscopy when a metal center with a nuclear spin momentum, like yttrium, is present.

Conclusions

We have demonstrated that the σ-yttrium–carbon bond in 14- and 16-electron permethylyttrocene carbyls is extremely reactive toward virtually all hydrogen-containing bonds. Our studies on the activation of CH bonds clearly indicate that a rich organometallic chemistry is available on the basis of reactions with the YC bonds.

The reaction mechanisms of these activation reactions as well as the hydrogenolysis of the YC bond are likely to proceed via four or five centered transition states. These σ-bond metathesis reactions are a convenient way for the synthesis of new salt-free[4] permethylyttrocene derivatives. The Lewis acidity of the metal center is high as is clearly shown by the complexation of polar solvent molecules and the presence of a γ-agostic interaction in **16**. The nuclear spin momentum is of yttrium is very helpful in the unequivocal interpretation of complicated NMR spectra.

In addition to stoichiometric reactions also catalytic reactions have been found in which the YC bond plays a crucial role. Examples are the dimerizations of α-alkynes and H/D exchange reactions between sp^2-CD and sp^3-CH bonds.

The reactivity of the hydrides toward unsaturated hydrocarbons, carbonyls, and ethers also promises an interesting chemistry, and we are currently exploring this field. The results of these studies will be reported in a subsequent paper.

Registry No. **1**, 95197-83-4; **2**, 109364-77-4; **3**, 109364-78-5; **4**, 109364-79-6; **5**, 109364-80-9; **6**, 109364-81-0; **7a**, 109364-82-1; **7b**, 109364-92-3; **7c**, 109364-93-4; **8**, 109364-83-2; **9**, 109364-84-3; **10**, 926-55-6; **11**, 62676-19-1; **12**, 90753-17-6; **13**, 109364-85-4; **14**, 109364-86-5; **15**, 109364-87-6; **16**, 108366-50-3; **17**, 109364-88-7; **18a**, 95099-09-5; **18b**, 109364-89-8; **19a**, 109364-90-1; **19b**, 109364-91-2; $(Cp_2^*YCl)_2$, 94348-89-7; $Cp_2^*YCl\cdot THF$, 94348-90-0; $CH_2(SiMe_3)_2$, 2117-28-4; $HC{\equiv}CSiMe_3$, 1066-54-2; propyne, 74-99-7; phenylethyne, 536-74-3; pyridine, 110-86-1; α-picoline, 109-06-8; mesitylene, 108-67-8.

Syntheses and Molecular and Electronic Structures of the μ_4-Methylidyne Clusters $[Fe_4(CO)_{12}C\cdot C(O)OCH_3]^-$ and $[Fe_4(CO)_{12}C\cdot C(O)CH_3]^-$: An Analysis of Steric and Bonding Effects

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The crystal, molecular, and electronic structures of $(C_2H_5)_4N[Fe_4(CO)_{12}C\cdot C(O)OCH_3]$, I, and $(C_2H_5)_4N[Fe_4(CO)_{12}C\cdot C(O)CH_3]$, II, which have served as the starting materials for a number of organometallic iron butterfly compounds, are described. Crystallographic data are as follows. I (296 K): space group *Pbca*, a = 12.079 (2) Å, b = 17.869 (4) Å, c = 27.692 (9) Å, Z = 8, R = 0.042, R_w = 0.055 for 2541 reflections ($I > 3\sigma(I)$), Mo Kα radiation. II (296 K): space group *Pbca*, a = 12.191 (7) Å, b = 17.296 (7) Å, c = 28.133 (7) Å, Z = 8; R = 0.037, R_w = 0.48 for 2932 reflections ($I > 2\sigma(I)$), Mo Kα radiation. Both cluster anions have an open butterfly core of four iron atoms with the methylidyne ligands $C\cdot CO_2CH_3$ (I) and $C\cdot C(O)CH_3$ (II) bound to all four metal atoms and the organic groups situated in the plane defined by the two backbone iron atoms and the methylidyne carbon atom. Comparisons are made between the molecular structures of I and II and those of the underivatized Fe_4C clusters. The differences between the two structure types are related to changes in the bonding between the μ_4-carbon and the iron framework. Interactive molecular graphics procedures were used to compute nonbonded atom–atom interaction energies as a probe of steric restrictions on the orientations of the carbomethoxy group in I and of the acetyl group in II. In both materials the organic groups are found to be sterically constrained to conformations close to those observed crystallographically. The observed slight tilt away from an axial orientation of the acetyl group in II is shown to mitigate steric repulsions between nonbonded atoms without disrupting strong orbital interactions between bonded atoms.

Introduction

The chemistry of the carbon atom in μ_4-carbido clusters has been of interest since the initial observations on the reactivity of the carbon atom in butterfly Fe_4C clusters.[1,2] This carbon atom forms bonds readily to carbon and to hydrogen, as in $[Fe_4(CO)_{12}C\cdot C(O)OCH_3]^-$[2] and $HFe_4(CO)_{12}CH$,[3] suggesting analogies with surface phenomena in metal-catalyzed CO hydrogenation. Several studies have been undertaken to determine the electronic structures of the Fe_4C family of cluster molecules and to correlate these with molecular structure and reactivity.[4-7] We have

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