Insertion Reactions into the σ-Yttrium–Carbon Bond. Molecular Structure of the Permethylyttrocene Iminoacyl Tetrahydrofuranate $(\eta^5\text{-}C_5Me_5)_2Y[\eta^2\text{-}C\{CH_2(3,5\text{-}Me_2C_6H_3)\}{=}N(2,6\text{-}Me_2C_6H_3)]\cdot C_4D_8O$

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The reactions of $Cp^*_2YCH(SiMe_3)_2$ (**1**) ($Cp^* = \eta^5\text{-}C_5Me_5$) with CO_2, *t*-BuCN, and *t*-BuNC give the monomeric complexes $Cp^*_2Y(\eta^2\text{-}O_2CCH(SiMe_3)_2)$ (**3**), $Cp^*_2YN{=}C(t\text{-}Bu)CH(SiMe_3)_2\cdot NC\text{-}t\text{-}Bu$ (**4**), and $Cp^*_2YCH(SiMe_3)_2\cdot CN\text{-}t\text{-}Bu$ (**5**), respectively. With CS_2 and (2,6-xylyl)NC no reaction is observed. The permethylyttrocene benzyl Cp^*_2YDMB (**2**) (DMB = 3,5-dimethylbenzyl) reacts with the substrates mentioned before and gives $Cp^*_2Y(\eta^2\text{-}O_2C(DMB))$ (**6**), $Cp^*_2Y(\eta^2\text{-}S_2C(DMB))$ (**7**), $Cp^*_2YN{=}C(DMB)\text{-}t\text{-}Bu\cdot NC\text{-}t\text{-}Bu$ (**8**), $Cp^*_2Y(\eta^2\text{-}C(DMB){=}N\text{-}t\text{-}Bu)\cdot CN\text{-}t\text{-}Bu$ (**9**), and $Cp^*_2Y(\eta^2\text{-}C(DMB){=}N(2,6\text{-xylyl}))$ (**10**) (xylyl = dimethylphenyl). The iminoacyl **10** reacts with THF to give the adduct $Cp^*_2Y(\eta^2\text{-}C(DMB){=}N(2,6\text{-xylyl}))\cdot THF$ (**11**). The crystal structure of **11** was determined by X-ray diffraction. The crystals of **11** are monoclinic, space group $P2_1/c$, with $a = 10.937$ (6) Å, $b = 18.367$ (8) Å, $c = 18.04$ (2) Å, $\beta = 104.58$ (6) Å, and $Z = 4$. The structure was refined to $R = 0.032$. The molecular structure of **11** clearly shows the η^2-coordination of the iminoacyl ligand with an Y–N distance of 2.407 (3) Å and an Y–C bond length of 2.392 (3) Å.

Introduction

For some time now, we have been engaged in studying the reactivity of the metal–carbon bond in coordinatively unsaturated early-transition-metal compounds. As a representative example, the work on titanocene derivatives Cp_2TiR ($Cp = \eta^5\text{-}C_5H_5$) and Cp^*_2TiR and especially their reactions toward small substrate molecules like CO, CO_2, CS_2, cyanides, and isocyanides is referred to.[1]

Recently we have extended our research to permethylyttrocene derivatives[2] and found that the σ-YC bond has a strong potential in CH activation reactions.[3] In this perspective we were anxious to investigate whether the 14-electron complexes Cp^*_2YR would activate unsaturated substrates like those mentioned above. We studied these reactions in some detail, concentrating on the nature and the properties of the newly formed complexes. In this paper we present the results of these investigations.

Experimental Section

Procedures, techniques, and instrumentation were as described previously.[2] The substrates CS_2 (Merck) and *t*-BuCN (Aldrich) were stored over molecular sieves (3 Å) under nitrogen before use. CO_2 was made by oxidation of CO (Matheson) over CuO. The isocyanides *t*-BuNC[4] and (2,6-xylyl)NC[5] were prepared according to the literature. The yttrocenes $Cp^*_2YCH(SiMe_3)_2$ (**1**)[2] and Cp^*_2YDMB (**2**)[3] were made as published before.

$Cp^*_2Y(\eta^2\text{-}O_2CCH(SiMe_3)_2)$ (3). A solution of 0.62 g of **1** (1.18 mmol) in 15 mL of benzene was exposed at room temperature to 3.04 mmol of CO_2 and stirred. After 3 h, 1.19 mmol of CO_2 (1.01 mol/mol of Y) was consumed, and the excess was removed. The solvent was evaporated and the colorless powder recrystallized from pentane (−80 °C). Isolated: 0.18 g of **3** (0.33 mmol, 27%). IR (cm^{-1}): 2720 (w), 1485 (m), 1455 (vs), 1380 (vs), 1365 (m), 1260 (m), 1245 (s), 1150 (m), 1060 (w), 1020 (m), 985 (m), 950 (m), 865 (s), 800 (w), 775 (m), 745 (w), 735 (m), 705 (w), 690 (m), 635 (m), 625 (m), 595 (w), 485 (m), 445 (m). Anal. Calcd for $C_{28}H_{49}YSi_2O_2$: C, 59.76; H, 8.78. Found: C, 59.95; H, 8.86.

$Cp^*_2YN{=}C(t\text{-}Bu)CH(SiMe_3)_2\cdot NC\text{-}t\text{-}Bu$ (4). A mixture of 0.54 g of **1** (1.04 mmol) and 0.25 mL of *t*-BuCN (2.32 mmol) in 10 mL of toluene was stirred at room temperature for 18 h. The clear solution was then stored at −80 °C, and colorless crystals were deposited. Yield: 0.54 g of **4** (0.78 mmol, 75%). IR (cm^{-1}): 2720 (w), 2265 (m), 1605 (vs), 1480 (m), 1365 (m), 1265 (m), 1245 (s), 1210 (w), 1190 (w), 1135 (m), 1035 (m), 1020 (m), 935 (m), 865 (s), 850 (vs), 830 (m), 800 (w), 705 (w), 665 (m), 595 (w), 475 (w). Anal. Calcd for $C_{37}H_{67}YN_2Si_2$: C, 64.87; H, 9.87. Found: C, 64.47; H, 9.63.

$Cp^*_2YCH(SiMe_3)_2\cdot CN\text{-}t\text{-}Bu$ (5). To a solution of 1.64 g of **1** (3.16 mmol) in 40 mL of Et_2O was added 0.78 mL of *t*-BuNC (6.85 mmol), and the mixture was stirred for 24 h at room temperature. The solvent and excess of *t*-BuNC were pumped off, and the solid was dissolved in 20 mL of Et_2O. Crystallization at −80 °C yielded 0.71 g of **5** (1.17 mmol, 37%) as white crystals. IR (cm^{-1}): 2720 (w), 2190 (s), 1485 (m), 1395 (m), 1370 (m), 1240 (m), 1230 (s), 1190 (m), 1115 (w), 1080 (w), 1050 (w), 1020 (m), 930 (w), 860 (s), 840 (s), 800 (w), 755 (m), 695 (m), 670 (m), 650 (m), 595 (m), 525 (w), 390 (m). Anal. Calcd for $C_{32}H_{58}YSi_2N$: C, 63.86; H, 9.71; Y, 14.77. Found: C, 63.33; H, 9.63; Y, 14.86.

$Cp^*_2Y(\eta^2\text{-}O_2C(DMB))$ (6). A stirred solution of 0.66 g of **2** (1.38 mmol) in 30 mL of pentane at −100 °C was exposed to 2.70 mmol of CO_2. Reaction took place immediately, and the yellow solution turned into a white suspension. After the solution was warmed to room temperature, the pentane and excess CO_2 were removed and the white solid was dissolved in hot toluene. After crystallization at −30 °C 0.37 g of **6** (0.71 mmol, 51%) was isolated as colorless crystals. IR (cm^{-1}): 3010 (w), 2720 (w), 1600 (s), 1570 (vs), 1490 (m), 1440 (vs), 1410 (s), 1365 (m), 1310 (m), 1260 (s), 1180 (w), 1160 (w), 1060 (w), 1020 (m), 960 (w), 920 (m), 900 (w), 845 (s), 800 (w), 745 (s), 725 (m), 680 (w), 640 (s), 595 (w), 570 (w), 540 (w), 420 (m), 380 (m). Anal. Calcd for $C_{30}H_{41}YO_2$: Y, 17.01; C, 68.95; H, 7.91. Found: Y, 16.81; C, 69.21; H, 8.08.

$Cp^*_2Y(\eta^2\text{-}S_2C(DMB))$ (7). A mixture of 0.46 g of **2** (0.95 mmol) and 0.07 mL of CS_2 (1.15 mmol) in 20 mL of pentane was stirred for 3 h at room temperature. After filtration the solution was concentrated until crystallization started and then was stored at −80 °C. The off-white crystals were isolated. Yield: 0.41 g of **7** (0.74 mmol, 78%). IR (cm^{-1}): 3010 (m), 2720 (w), 1595 (s), 1510 (w), 1480 (m), 1430 (m), 1365 (m), 1300 (w), 1260 (w), 1205 (s), 1155 (w), 1075 (s), 1020 (s), 1000 (m), 945 (m), 900 (w), 865 (s), 855 (s), 800 (w), 720 (s), 620 (m), 595 (w), 550 (w), 520 (w), 350 (m). Anal. Calcd for $C_{30}H_{41}YS_2$: C, 64.96; H, 7.45. Found: C, 65.07; H, 7.68.

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[1] (a) de Boer, E. J. M.; Teuben, J. H. *J. Organomet. Chem.* **1977**, *140*, 41. (b) de Boer, E. J. M.; Teuben, J. H. *J. Organomet. Chem.* **1979**, *166*, 193. (c) Klei, E.; Teuben, J. H. *J. Organomet. Chem.* **1980**, *188*, 97. (d) Klei, E.; Teuben, J. H.; de Liefde Meijer, H. J. *J. Chem. Soc., Chem. Commun.* **1981**, 342. (e) Klei, E.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *222*, 79. (f) Teuben, J. H. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragala, J. L., Eds.; D. Reidel: Dordrecht, 1985.

[2] den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726.

[3] den Haan, K. H.; Wielstra, Y.; Teuben, J. H., submitted for publication in *Organometallics*.

[4] Weber, W. P.; Gohel, G. W.; Ugi, I. K. *Angew. Chem.* **1972**, *84*, 587.

[5] Shingaki, T.; Takebayaski, M. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 617.

0276-7333/87/2306-1509\$01.50/0

Cp*$_2$YN=C(DMB)-*t*-Bu·NC-*t*-Bu (8). A mixture of 1.66 g of **2** (3.48 mmol) and 0.76 mL of *t*-BuCN (7.97 mmol) in 30 mL of Et_2O was stirred for 24 h at room temperature. After filtration the clear solution was stored overnight at −80 °C and colorless crystals were deposited. Yield: 1.32 g of **8** (2.05 mmol, 58%). IR (cm^{-1}): 3020 (m), 2720 (w), 2255 (m), 1670 (s), 1655 (m), 1605 (m), 1485 (m), 1360 (m), 1315 (w), 1285 (w), 1235 (m), 1200 (w), 1155 (w), 1040 (m), 1025 (m), 995 (m), 935 (w), 850 (w), 830 (w), 800 (w), 780 (m), 690 (m), 650 (w), 595 (w), 525 (w), 475 (w), 390 (m). Anal. Calcd for $C_{39}H_{59}YN_2$: C, 72.65; H, 9.22; Y, 13.79. Found: C, 72.69; H, 9.20; Y, 13.79.

Cp*$_2$Y(η^2-C(DMB)=N-*t*-Bu)·CN-*t*-Bu (9). A mixture of 0.87 g of **2** (1.81 mmol) and 0.41 mL of *t*-BuNC (3.61 mmol) in 35 mL of Et_2O was stirred for 24 h at room temperature. The color changed from orange to pale yellow. Off-white crystals formed on storing the clear solution at −80 °C. Isolated: 0.39 g of **9** (0.66 mmol, 34%). IR (cm^{-1}): 3020 (m), 2720 (w), 2190 (s), 1610 (m), 1530 (m), 1490 (m), 1400 (w), 1390 (w), 1375 (m), 1365 (m), 1260 (w), 1240 (m), 1225 (m), 1195 (s), 1150 (w), 1030 (w), 1015 (m), 950 (w), 920 (w), 860 (m), 840 (s), 800 (w), 755 (w), 700 (m), 680 (m), 595 (w), 525 (w), 440 (m), 360 (m). Anal. Calcd for $C_{39}H_{59}YN_2$: C, 72.65; H, 9.22; Y, 13.79. Found: C, 73.02; H, 9.29; Y, 13.77.

Cp*$_2$Y(η^2-C(DMB)=N(2,6-xylyl)) (10). Et_2O (40 mL) was condensed onto a mixture of 0.53 g of **2** (1.12 mmol) and 0.15 g of (2,6-xylyl)NC (1.13 mmol) at −80 °C. After being warmed to room temperature and stirred for 20 h, the mixture was filtered and the clear yellow solution stored at −80 °C to give 0.34 g of **10** (0.55 mmol, 50%) as pale yellow crystals. IR (cm^{-1}): 3020 (m), 2720 (w), 1595 (m), 1505 (w), 1490 (s), 1480 (m), 1410 (w), 1365 (m), 1310 (w), 1245 (w), 1160 (m), 1090 (m), 1050 (m), 1020 (m), 955 (w), 835 (s), 810 (m), 800 (w), 770 (s), 760 (s), 695 (m), 660 (m), 625 (w), 595 (w), 555 (w), 495 (m), 435 (m), 380 (m). Anal. Calcd for $C_{38}H_{50}YN$: C, 74.86; H, 8.27; Y, 14.58. Found: C, 74.62; H, 8.27; Y, 14.86.

Cp*$_2$Y(η^2-C(DMB)=N(2,6-xylyl)·THF-*d*$_8$ (11). A solution of 0.25 g of **10** (0.36 mmol) in 1.2 mL of THF-*d*$_8$ was stored overnight at −40 °C. The crystals formed were isolated. Yield: 0.12 g of **11** (0.17 mmol, 48%). IR (cm^{-1}): 3020 (m), 2720 (w), 2225 (w), 2110 (w), 1595 (m), 1550 (s), 1480 (m), 1420 (m), 1420 (m), 1365 (m), 1345 (m), 1310 (w), 1295 (m), 1265 (w), 1160 (m), 1090 (m), 1045 (w), 1020 (m), 1005 (s), 975 (m), 860 (w), 825 (m), 810 (m), 800 (w), 775 (m), 760 (s), 750 (m), 715 (m), 685 (s), 660 (m), 650 (w), 595 (w). Anal. Calcd for $C_{42}H_{50}D_8YNO$: C, 73.12; H/D, 9.64. Found: C, 72.93; H/D, 9.61.

Structure Determination and Refinement of 11. A suitable, pale yellow crystal of **11** was selected in a glovebox, mounted on a glass fiber, and transferred into the cold nitrogen stream of the low-temperature unit of an Enraf-Nonius CAD4F diffractometer. Crystal data and other details of the structure determination are collected in Table I. Unit cell parameters and their standard deviations were determined from a least squares of the setting angles of 19 reflections in the range 9.0° < θ < 11.7°. Reduced cell calculation did not indicate any higher lattice symmetry.[6] The intensity data were corrected for decay, Lorentz, and polarization effects. Variance $\sigma^2(I)$ was calculated on the basis of counting statistics and the term $(PI)^2$ where P is the instability constant.[7] The position of the yttrium atom was located from a Patterson map. The non-hydrogen atom positions were obtained with DIRDIF.[8] At this stage an empirical correction was applied by using DIFABS.[9] Hydrogen atoms were located from a difference Fourier synthesis. The structure is affected by some disorder in the THF ring, which involves carbon atom C(41). Population refinement of two sites revealed equal site-occupation factors. Finally the occupation factors were fixed (0.5). The corresponding hydrogen atoms were introduced at calulated positions (C–H = 1.00 Å) and refined with fixed geometry with respect to their parent atoms (C(411) and C(412)). Refinement on F by block-diagonal least-squares techniques converged at R = 0.032. All non-hydrogen atoms were refined with anisotropic thermal parameters. A single isotropic thermal parameter for all hydrogen atoms was used for the refinement. The final values of the refined positional parameters are presented in Table II. Scattering factors were taken from ref 10 and anomalous dispersion corrections from ref 11. All calculations were carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program XTAL,[12] the EUCLID package,[13] and a local modified version of PLUTO.

Table I. Crystal Data and Details of the Structure Analysis of Cp*$_2$Y(η^2-C(DMB)=N(2,6-xylyl))•THF-*d*$_8$ (11)

(a) Crystal Structure	
empirical formula	$C_{42}H_{50}D_8NOY$
mol wt	689.74
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a, Å	10.937 (6)
b, Å	18.367 (8)
c, Å	18.04 (2)
β, deg	104.58 (6)
V, Å^3	3507 (5)
Z	4
D_{calcd}, g/cm^3	1.307
$F(000)$, electrons	1456
μ(Mo Kα), cm^{-1}	17.6
approx cryst dimens, mm	0.25 × 0.2 × 0.2
(b) Data Collection	
temp, K	120
radiatn, Å	Mo K$\bar{\alpha}$ (λ = 0.71073) graphite monochrom
θ_{min}, θ_{max}, deg	1.1, 25.0
scan width, deg	0.80 + 0.35 tan θ
hor and vert aperture	3.2, 4.0
max time/relfectn, s	80
cryst to detector, mm	173
data set	±12,21,±21
std reflctns	$\bar{2}7\bar{2}$, 440, 046
decay correctn	0.928–1.014
absorptn correctn	empirical
X-ray exposure time, h	355.1
total data	12654
total unique	6125
obsd data, $F > 4\sigma(F)$	4052
(c) Refinement	
no. of reflections	4052
no. of parameters varied	584
R	0.032
ωR	0.036
ω^{-1}	$\sigma^2(F)$
S	1.266
$(\Delta/\sigma)_{av}$	0.018
$(\Delta/\sigma)_{max}$	0.737
min and max dens, e/Å^3	−0.422 and 0.402

Results and Discussion

I. General Considerations. This paper deals with reactions of unsaturated substrates (S) with σ-YC bonds in monomeric Cp*$_2$YR complexes (R = $CH(SiMe_3)_2$ (**1**),[2] DMB (**2**)[3]). The reactions are most likely to proceed via adducts Cp*$_2$YR·S[1] (eq 1). In these adduct intermediates

$$Cp^*_2YR + S \rightarrow Cp^*_2YR{\cdot}S \qquad (1)$$

the substrate and the YC bond are activated and a mi-

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(6) Le Page, Y. *J. Appl. Cryst.* **1982**, *15*, 255.

(7) McCandlish, L. E.; Stout, G. H.; Andrews, L. C. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1975**, *A31*, 245.

(8) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; van der Hark, Th. E. M.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G.; Parthasarathi, V.; Bruins Slot, H. J.; Haltiwanger, R. C. DIRDIF, Program for structure solution knowing partial structure, Technical Report 1984/1, 1984; Crystallographic Laboratory, University of Nijmegen, Nijmegen, The Netherlands.

(9) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1983**, *A39*, 158.

(10) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

(11) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(12) Stewart, J. H.; Hall, S. R. The XTAL system, Technical Report TR-1364, 1983; Computer Science Center, University of Maryland, College Park, MD.

(13) Spek, A. L. In *Computational Crystallography*, Sayre, D., Ed.; Clarendon: Oxford, 1982; p 528.

Table II. Final Positional Parameters of the Non-Hydrogen Atoms of $Cp^*_2Y(\eta^2\text{-}C(DMB){=}N(2,6\text{-xylyl}))\bullet THF\text{-}d_8$ and Equivalent Isotropic Temperature Factors

atom	x	y	z	U(eq), Å^2
Y(1)	0.86723 (3)	0.11059 (2)	0.19598 (2)	0.0094 (1)
O(1)	0.9789 (2)	0.0530 (1)	0.3177 (1)	0.0153 (6)
N(1)	0.6895 (2)	0.0775 (1)	0.2449 (1)	0.0120 (6)
C(1)	0.9691 (3)	0.2367 (2)	0.1610 (2)	0.017 (1)
C(2)	0.8444 (3)	0.2553 (2)	0.1629 (2)	0.016 (1)
C(3)	0.8364 (3)	0.2522 (2)	0.2399 (2)	0.015 (1)
C(4)	0.9565 (3)	0.2318 (2)	0.2859 (2)	0.014 (1)
C(5)	1.0383 (3)	0.2210 (2)	0.2363 (2)	0.015 (1)
C(6)	1.0232 (3)	0.2510 (2)	0.0937 (2)	0.028 (1)
C(7)	0.7456 (3)	0.2855 (2)	0.0964 (2)	0.024 (1)
C(8)	0.7246 (3)	0.2777 (2)	0.2671 (2)	0.024 (1)
C(9)	0.9982 (3)	0.2363 (2)	0.3716 (2)	0.023 (1)
C(10)	1.1793 (3)	0.2112 (2)	0.2609 (2)	0.022 (1)
C(11)	1.0002 (3)	0.0527 (2)	0.1009 (2)	0.019 (1)
C(12)	0.9954 (3)	-0.0040 (2)	0.1531 (2)	0.019 (1)
C(13)	0.8687 (3)	-0.0270 (2)	0.1403 (2)	0.015 (1)
C(14)	0.7956 (3)	0.0151 (2)	0.0801 (2)	0.015 (1)
C(15)	0.8752 (3)	0.0651 (2)	0.0558 (2)	0.018 (1)
C(16)	1.1208 (4)	0.0797 (2)	0.0849 (2)	0.036 (1)
C(17)	1.1097 (3)	-0.0413 (2)	0.2020 (2)	0.033 (1)
C(18)	0.8231 (3)	-0.0935 (2)	0.1736 (2)	0.026 (1)
C(19)	0.6607 (3)	-0.0011 (2)	0.0382 (2)	0.024 (1)
C(20)	0.8354 (4)	0.1124 (2)	-0.0141 (2)	0.033 (1)
C(21)	0.6439 (3)	0.1132 (2)	0.1819 (2)	0.014 (1)
C(22)	0.5038 (3)	0.1306 (2)	0.1572 (2)	0.020 (1)
C(23)	0.4637 (3)	0.1907 (2)	0.0986 (2)	0.016 (1)
C(24)	0.4004 (3)	0.2519 (2)	0.1149 (2)	0.018 (1)
C(25)	0.3584 (3)	0.3058 (2)	0.0606 (2)	0.018 (1)
C(26)	0.3830 (3)	0.2985 (2)	-0.0108 (2)	0.019 (1)
C(27)	0.4472 (3)	0.2381 (2)	-0.0283 (2)	0.018 (1)
C(28)	0.4866 (3)	0.1847 (2)	0.0265 (2)	0.016 (1)
C(29)	0.2877 (3)	0.3709 (2)	0.0790 (2)	0.027 (1)
C(30)	0.4749 (3)	0.2306 (2)	-0.1058 (2)	0.027 (1)
C(31)	0.6148 (3)	0.0542 (2)	0.2962 (2)	0.012 (1)
C(32)	0.5216 (3)	-0.0001 (2)	0.2761 (2)	0.014 (1)
C(33)	0.4498 (3)	-0.0167 (2)	0.3281 (2)	0.018 (1)
C(34)	0.4704 (3)	0.0174 (2)	0.3975 (2)	0.022 (1)
C(35)	0.5672 (3)	0.0671 (2)	0.4192 (2)	0.019 (1)
C(36)	0.6411 (3)	0.0855 (2)	0.3695 (2)	0.015 (1)
C(37)	0.4971 (3)	-0.0421 (2)	0.2026 (2)	0.022 (1)
C(38)	0.7474 (3)	0.1388 (2)	0.3966 (2)	0.021 (1)
C(39)	1.1111 (3)	0.0602 (2)	0.3584 (2)	0.026 (1)
C(40)	1.1450 (2)	-0.0073 (2)	0.4074 (2)	0.030 (1)
C(42)	0.9253 (3)	-0.0054 (2)	0.3529 (2)	0.026 (1)
C(412)	1.0183 (6)	-0.0193 (4)	0.4277 (4)	0.028 (2)

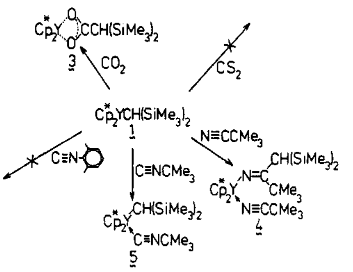
gratory insertion reaction can take place. When the activations do not occur, the adduct can be isolated as has been demonstrated for titanium,[1b,14] but in general only the insertion products are obtained. In the reactions described below the Cp* ligands are not involved. The IR (cf. Experimental Section) and NMR (^{1}H, Table III; ^{13}C, Table IV) spectra all show the characteristics of π-bonded Cp* ligands.

Substrates that contain a carbonyl function, like CO, ketones, and metal carbonyls ($M(CO)_n$), are excluded from the discussion here. These reactions, which certainly are within the scope of this paper, are interesting and unexpected. They are still under investigation at this moment.

II. Reactions of $Cp^*_2YCH(SiMe_3)_2$ (1). The reactions of 1 with CO_2, CS_2, *t*-BuCN, *t*-BuNC, and (2,6-xylyl)NC are presented in Scheme I.

With CO_2 the bis(trimethylsilyl)acetate yttrocene $Cp^*_2Y(\eta^2\text{-}O_2CCH(SiMe_3)_2)$ (3) is formed. This clearly demonstrates the ability of the YC bond to activate CO_2. Remarkable is that with CS_2 no reaction was observed (stirring for 48 h at 25 °C). A probable reason for this is that a CS_2 adduct cannot be formed with 1. In their review on CS_2 activation, Butler and Fenster[15] showed that σ-bonded CS_2 complexes are very rare compared to π-bonded complexes. In 1 the large Cp* and hydrocarbyl ligands fill the coordination sphere around yttrium almost completely and the favored π-coordination of CS_2 cannot be achieved.

Scheme I



The reaction of 1 with *t*-BuCN gives the anticipated formation of an imide complex.[16] Surprisingly this yttrocene imide coordinates a second nitrile molecule to give the 16-electron complex $Cp^*_2YN{=}C(t\text{-}Bu)CH(SiMe_3)_2\cdot NC\text{-}t\text{-}Bu$ (4).

Complexation of the substrate is also observed in the reaction of 1 with *t*-BuNC. Insertion of the isocyanide into the YC bond, however, does not take place (stirring 24 h at 25 °C), and the adduct $Cp^*_2YCH(SiMe_3)_2\cdot CN\text{-}t\text{-}Bu$ (5) is isolated. Thus, the rodlike isocyano part of the ligand appears to fit into the coordination sphere of 1, but the transition state for insertion[17] cannot be achieved. With (2,6-xylyl)NC no reaction occurred, owing to blocking of the coordination site on the metal.[2]

The spectroscopic properties of the complexes 3 and 4 strongly resemble those of their Ti[1] and Sc[16] analogues, apart from the characteristics of the $SiMe_3$ moieties.[2] The spectra of 5, however, deserve further comment.

The IR spectrum of 5 is almost superimposable on that of the starting complex 1, except for the absorptions at 2190 (s), 1395 (m), 1190 (m), and 860 (m) cm^{-1}, which are tentatively assigned to the $\nu_{C\equiv N}$, ν_{C-C}, ν_{C-N}, and δ_{C-C} of the coordinated isocyanide, respectively. The $\nu_{C\equiv N}$ is shifted to higher energy ($\Delta(\nu_{C\equiv N}) = +53$ cm^{-1}), with respect to the free ligand, which indicates σ-coordination of the isocyanide.[1b] The $\Delta(\nu_{C\equiv N})$ is larger than those observed in titanocene adducts, which is easily explained by the complete impossibility of π-back-donation[18] in yttrocene complexes as no d electrons are present.

The NMR spectra of 5 (Tables I and II) also resemble those of 1 except again for the isocyanide signals. An aspect worth mentioning is the $^1J_{CH}$ coupling constant (106.9 Hz) on the ligating methyl carbon of the $CH(SiMe_3)_2$ ligand σ-bonded to yttrium (δ 24.17) in the $^{13}C\{^1H\}$ NMR spectrum. This coupling constant is 23 Hz larger than the corresponding value in 1, indicating that in the 16-electron complex 5 the α-agostic interaction, which has been irrefutably established for 1,[2] is no longer present.

From the results described above it is clear that the steric bulk of the $CH(SiMe_3)_2$ ligand has a decisive influence on the reactivity of the YC bond.

III. Reactions of Cp^*_2YDMB (2). In complex 2 the steric influence of the ligand is assumed to be less compared with that of 1. Here the carbon bonded to yttrium is only monosubstituted by an organic group, which increases the possibility of substrate coordination. The

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(14) de Boer, E. J. M.; ten Cate, L. C.; Staring, A. G. J.; Teuben, J. H. *J. Organomet. Chem.* **1979**, *181*, 61.

(15) Butler, I. S.; Fenster, A. E. *J. Organomet. Chem.* **1974**, *66*, 161.

(16) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443.

(17) Treichel, P. M. *Adv. Organomet. Chem.* **1973**, *11*, 21.

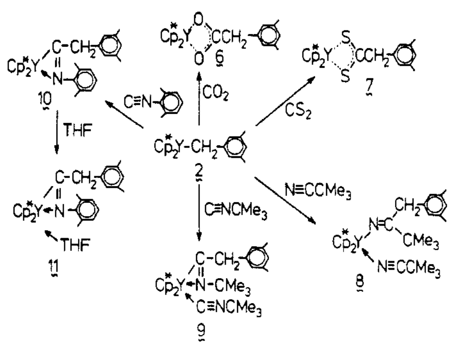
(18) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, 1978; p 269.

Table III. ^{1}H NMR Data of the New Permethylyttrocene Compounds[a]

complex	C_5Me_5	R	L
3	1.87 (s, 30 H)	0.31 (s, 18 H, $SiMe_3$) 1.67 (s, 1 H, $CHSi_2$)	. . .
4	2.07 (s, 30 H)	0.32 (s, 18 H, $SiMe_3$) 1.23 (s, 9 H, CMe_3) 2.35 (s, 1 H, $CHSi_2$)	0.87 (s, 9 H, CMe_3)
5	2.03 (s, 15 H) 2.07 (s, 15 H)	−0.44 (d, 1 H, $^2J_{YH}$ = 2.3 Hz, YCH) 0.36 (s, 18 H, $SiMe_3$)	0.94 (s, 9 H, CMe_3)
6[b]	1.85 (s, 30 H)	2.35 (s, 6 H, 3,5-Me) 3.60 (s, 2 H, CH_2) 6.93 (s, 1 H, *p*-H) 7.18 (s, 2 H, *o*-H)	
7	1.85 (s, 30 H)	2.19 (s, 6 H, 3,5-Me) 4.40 (s, 2 H, CH_2) 6.78 (s, 1 H, *p*-H) 7.17 (s, 2 H, *o*-H)	
8	2.02 (s, 30 H)	1.22 (s, 9 H, CMe_3) 2.32 (s, 6 H, 3,5-Me) 3.73 (s, 2 H, CH_2) 6.79 (s, 1 H, *p*-H) 7.12 (s, 2 H, *o*-H)	0.72 (s, 9 H, CMe_3)
9	1.99 (s, 30 H)	1.43 (s, 9 H, CMe_3) 2.40 (s, 6 H, 3.5-Me) 4.10 (s, 2 H, CH_2) 6.91 (s, 1 H, *p*-H) 7.93 (s, 2 H, *o*-H)	1.00 (s, 9 H, CMe_3)
10	1.94 (s, 30 H)	2.11 (s, 6 H, 2,6-Me) 2.29 (s, 6 H, 3.5-Me) 3.73 (s, 2 H, CH_2) 6.80 (s, 1 H, *p*-H_{DMB}) 6.99 (br s, 3 H, *m*,*p*-H_{xylyl}) 7.11 (s, 2 H, *o*-H_{DMB})	

[a] 90-MHz ^{1}H NMR spectra in C_6D_6 at 20 °C, δ, δ(Me_4Si) 0.0. [b] In $CDCl_3$ at 20 °C.

Scheme II



isolation of the THF adduct of 2, Cp*$_2$YDMB·THF,[3] clearly demonstrates this. For 1 a THF adduct cannot be obtained. We therefore performed the reactions of 2 with the same substrates as described above. The results of these reactions are given in Scheme II.

The insertion of CO_2 to give the carboxylate complex **6** is not surprising knowing the result of the same reaction of **1**. More exciting is the activation of CS_2 as it reacts with **2** and the dithiocarboxylato complex Cp*$_2$Y(η^2-S_2C-(DMB))[19] (**7**) is formed. Thus, it appears that in **2** sufficient space is available for the initial formation of a π-CS_2 adduct in which the CS and YC bonds are activated.[17]

The reaction of **2** with *t*-BuCN proceeds identical with that of **1** with *t*-BuCN and the yttrocene imide cyanide adduct Cp*$_2$YN=C(DMB)*t*-Bu·NC-*t*-Bu (**8**) is formed.

Toward isocyanides **2** behaves more interestingly than **1**. It appears that the transition state for insertion[17] now can be achieved as insertion products like the iminoacyls **9** and **10** are formed. Remarkable is that for *t*-BuCN a second isocyanide molecule coordinates to yttrium and the 18-electron adduct Cp*$_2$Y(η^2-C(DMB)=N-*t*-Bu)·CN-*t*-Bu (**9**) is obtained. When the steric bulky isocyanide (2,6-xylyl)NC reacts with **2**, this is not observed and only the 16-electron iminoacyl Cp*$_2$Y(η^2-C(DMB)=N(2,6-xylyl)) **10** is isolated. In **10**, however, the coordinative unsaturation can be reduced by a smaller Lewis base; e.g., with THF the 18-electron Cp*$_2$Y(η^2-C(DMB)=N(2,6-xylyl))·THF (**11**) is formed.

The spectroscopy of the insertion products of **2** shows all the expected characteristics of these compounds, and a detailed discussion seems not appropriate. The only feature for which the spectroscopy does not allow an unequivocal assignment is the bonding of the iminoacyl ligands in **9**, **10**, and **11**. In the IR spectra of these complexes $\nu_{C=N}$ vibration modes are observed at 1530, 1490, and 1550 cm^{-1}, respectively. According to Adams[20] these wavenumbers are indicative for η^1-coordination. Contradictory to this is the observation by van Bolhuis et al.[21] that in Cp_2Ti(η^2-C(Ph)=(2,6-xylyl) the iminoacyl is η^2-bonded to titanium. For the latter complex $\nu_{C=N}$ is observed at 1573 cm^{-1}. Thus, IR spectroscopy alone does not allow to discriminate between the various bonding modes of the iminoacyl ligand.

The ^{13}C NMR spectra of **9** and **10** show the iminoacyl carbon resonances at δ 257.40 ($^1J_{YC}$ = 23.2 Hz) and 268.55 ($^1J_{YC}$ = 30.3 Hz), respectively. These extreme low-field shifts indicate η^2-bonding of the iminoacyl ligand,[1b,20] which leaves, with respect to the IR data, an ambiguous situation to be settled. This point is clarified by an X-ray determination of the molecular structure of **11**. This complex was chosen because of the steric crowding in this molecule. We anticipated that if η^2-coordination is present in **11**, this

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[19] In the IR spectrum of 7 the ν_{CS} is observed at 940 cm^{-1}, which indicates η^2-bonding. Arduini, A. L.; Takats, J. *Inorg. Chem.* **1981**, *20*, 2480.

[20] Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1977**, *99*, 6544.

[21] van Bolhuis, F.; de Boer, E. J. M.; Teuben, J. H. *J. Organomet. Chem.* **1979**, *170*, 299.

Table IV. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR Spectra of the New $\mathrm{Cp^*_2YR}$ Complexes

complex	C_5Me_5	$C_5\mathrm{Me}_5$	R/L
3	10.72 (q, 125.4)	117.84 (s)	2.15 (q, 119.4, $\mathrm{SiMe_3}$) 30.61 (d, 103.4, C*C*H) 187.17 (s, $\mathrm{YO_2}C$)
5	12.60 (q, 125.2) 12.91 (q, 125.3)	117.48 (s) 118.00 (s)	7.19 (q, 116.8, $\mathrm{SiMe_3}$) 24.17 (dd, 106.9, $^1J_{\mathrm{YC}}$ = 34.2, Y*C*H) 29.14 (q, 129.6, $\mathrm{C}Me_3$) 56.56 (s, $C\mathrm{Me_3}$) 149.27 (d, $^1J_{\mathrm{YC}}$ = 10.9, $\mathrm{Y{\leftarrow}C{\equiv}N}$)
6[b]	11.22 (q, 125.5)	117.12 (s)	21.60 (q, 126.2, 3,5-Me) 47.02 (t, 127.0, $\mathrm{CH_2}$) 127.86 (d, 154.3, *o*-C) 128.36 (d, 156.4, *p*-C) 134.65 (s, *m*-C) 137.78 (s, α-C) 180.61 (s, $\mathrm{YO_2C}$)
7	10.97 (q, 125.6)	118.13 (s)	21.27 (q, 126.0, 3,5-Me) 64.29 (t, 131.6, $\mathrm{CH_2}$) 127.84 (d, 156.4, *o*-C) 128.91 (d, 155.9, *p*-C) 137.67 (s, *m*-C) 138.07 (s, α-C) 255.59 (d, $^2J_{\mathrm{YC}}$ = 19.8, $\mathrm{YS_2C}$)
8	11.66 (q, 124.7)	114.13 (s)	21.51 (q, 125.7, 3,5-Me) 27.14 (q, 125.6, $\mathrm{N{\equiv}CC}Me_3$) 28.08 (t, 133.6, $\mathrm{CH_2}$) 29.84 (q, 124.7, $\mathrm{-N{=}CC}Me_3$) 43.08 (q, $\mathrm{N{\equiv}C}C\mathrm{Me_3}$) 45.12 (s, $\mathrm{-N{=}C}C\mathrm{Me_3}$) 127.16 (d, 153.9, *p*-C) 127.64 (d, 156.1, *o*-C) 130.64 (s, $\mathrm{Y{\leftarrow}N{\equiv}C}$) 136.99 (s, *m*-C) 141.65 (s, α-C) 168.96 (d, $^2J_{\mathrm{YC}}$ = 9.8, $\mathrm{Y{-}N{=}C}$)
9	12.18 (q, 124.5)	113.62 (s)	21.50 (q, 125.8, 3,5-Me) 29.36 (q, 129.8, $\mathrm{{\equiv}NC}Me_3$) 31.95 (q, 126.6, $\mathrm{{=}NC}Me_3$) 45.19 (t, 122.3, $\mathrm{CH_2}$) 55.57 (s, $\mathrm{{\equiv}N}C\mathrm{Me_3}$) 57.94 (s, $\mathrm{CN}C\mathrm{Me_3}$) 127.48 (d, 158.1, *p*-C) 128.61 (d, 154.0, *o*-C) 137.34 (s, *m*-C) 141.94 (s, α-C) 155.29 (d, $^1J_{\mathrm{YC}}$ = 7.5, $\mathrm{Y{\leftarrow}C{\equiv}N}$) 257.40 (d, $^1J_{\mathrm{YC}}$ = 23.2, $\mathrm{Y{-}C{=}N}$)
10[c]	12.67 (q, 124.6)	116.29 (s)	20.40 (q, 126.4, 2,6-Me) 21.42 (q, 125.8, 3,5-Me) 47.92 (t, 122.4, $\mathrm{CH_2}$) 124.30 (d, 159.4, *p*-$\mathrm{C_{DMB}}$) 127.66 (d, 154.2, *p*-$\mathrm{C_{xylyl}}$) 128.88 (d, 158.2, *m*-$\mathrm{C_{xylyl}}$) 129.02 (d, 153.3, *o*-$\mathrm{C_{DMB}}$) 129.77 (s, *o*-$\mathrm{C_{xylyl}}$) 137.49 (s, *m*-$\mathrm{C_{DMB}}$) 140.60 (s, α-$\mathrm{C_{DMB}}$) 150.31 (s, α-$\mathrm{C_{xylyl}}$) 268.55 (d, $^1J_{\mathrm{YC}}$ = 30.3, $\mathrm{Y{-}C{=}N}$)

[a] 50.3-MHz $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectra in $\mathrm{C_6D_6}$ at 20 °C, δ, δ($\mathrm{Me_4Si}$) 0.0, multiplicity and coupling constants $^1J_{\mathrm{CH}}$ (Hz) in parentheses. [b] In $\mathrm{CDCl_3}$ at 20 °C. [c] In THF-d_8 at 20 °C.

bonding mode will undoubtedly also occur in the other iminoacyl complexes.

IV. The Molecular Structure of $\mathrm{Cp^*_2Y(\eta^2\text{-}C(DMB){=}N(2,6\text{-}xylyl))\cdot THF}$-$d_8$ (11). The molecular structure of **11** shows a typical example of a bent metallocene derivative[22] with an iminoacyl group and a THF-d_8 molecule as additional ligands (Figure 1). The staggered Cp* ligands are bonded to the yttrium atom in η^5 fashion with an average Y(1)–C(η^5) distance of 2.728 (4) Å (Table V). The Y(1)–C(η^5) distances observed in **11** (2.685 (3)–2.782 (3) Å) are considerably longer than observed in other permethylyttrocenes: $\mathrm{Cp^*_2Y(\mu\text{-}Cl)YClCp^*_2}$[23] [2.56 (2)–2.69 (2) Å], $\mathrm{Cp^*_2YN(SiMe_3)_2}$[2] [2.632 (7)–2.737 (7) Å], and **1** [2.637 (6)–2.692 (6) Å]. A plausible explanation for these longer bond lengths is that the $\mathrm{Y^{3+}}$ radius is larger in a formally 18-electron complex like **11** than in the other 14- and 16-electron compounds. The metal–ring centroid ($\mathrm{Cp^0}$) distances are Y(1)–$\mathrm{Cp^0}$(1) = 2.464 (3) Å and Y(1)–$\mathrm{Cp^0}$(2) = 2.434 (3) Å; the $\mathrm{Cp^0}$(1)–Y(1)–$\mathrm{Cp^0}$(2) angle is 132.0 (5)°, which is comparable with those observed in **1** of 134.4 (4)° and in $\mathrm{Cp^*_2YN(SiMe_3)_2}$ of 132.4 (2) and 132.2 (2)°.

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(22) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1726.

(23) Evans, W. J.; Peterson, T. T.; Rausch, M. D.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1985**, *4*, 554.

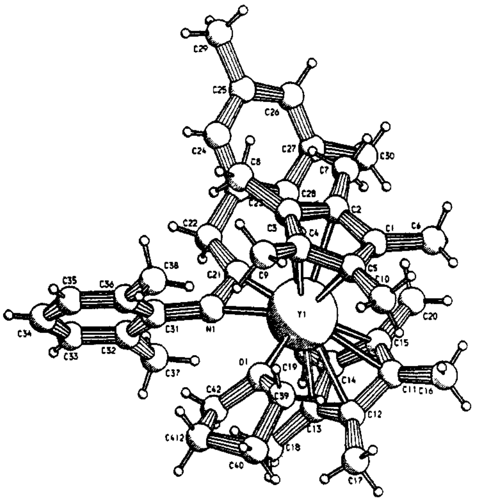

Figure 1. The molecular structure of Cp*$_2$Y(η^2-C(DMB)=N-(2,6-xylyl))·THF-d_8 (11).

Table V. Selected Interatomic Distances (Å) for Cp*$_2$Y(η^2-C(DMB)=N(2,6-xylyl))•THF-d_8 (11)

Cp*(1) [C(1)–C(10)]		Cp*(2) [C(11)–C(20)]	
⟨Y(1)–C(η^5)⟩	2.742 (3)	⟨Y(1)–C(η^5)⟩	2.714 (4)
Y(1)–Cp^0(1)	2.464 (4)	Y(1)–Cp^0 (2)	2.434 (5)
⟨C–C⟩$_{ring}$	1.416 (5)	⟨C–C⟩$_{ring}$	1.413 (5)
⟨C–CH$_3$⟩	1.502 (5)	⟨C–CH$_3$⟩	1.503 (5)
iminoacyl		THF	
Y(1)–N(1)	2.407 (3)	Y(1)–O(1)	2.466 (3)
Y(1)–C(21)	2.392 (3)	O(1)–C(39)	1.454 (4)
N(1)–C(21)	1.299 (4)	O(1)–C(42)	1.444 (4)
N(1)–C(31)	1.444 (5)	C(39)–C(40)	1.513 (5)
C(21)–C(22)	1.518 (4)	C(40)–C(41)	1.537 (8)
		C(41)–C(42)	1.493 (7)
DMB		2,6-Xylyl	
C(22)–C(23)	1.514 (4)	⟨C–C⟩$_{ring}$	1.391 (5)
⟨C–C⟩$_{ring}$	1.388 (5)	C(32)–C(37)	1.499 (5)
C(25)–C(29)	1.505 (5)	C(36)–C(38)	1.504 (4)
C(27)–C(30)	1.510 (5)		

[a] Cp^0 = ring centroid.

There is no evidence of localization of the π-electron density in the Cp* rings. The mean values of the (C–C)$_{ring}$ distances are 1.416 (5) Å for Cp*(1) and 1.413 (5) Å for Cp*(2). The average bond angles in the rings are 108.0 (3)° for both ligands. The mean values of ring to methyl carbon bond, C–C, are 1.502 (5) and 1.503 (5) Å in the Cp*(1) and Cp*(2) ligands, respectively. The two Cp* ligands are dished; the methyl carbon atoms are out of the ring plane exo to the metal center (displacements are between 0.17 (3) and 0.35 (3) Å).

The THF molecule is coordinated in such a way that it fills nicely the open space around the yttrium atom. The Y(1)–O(1) bond length, 2.466 (3) Å, almost equals the distances observed in (Cp′$_2$YH·THF)$_2$[24] (Cp′ = η^5-C$_5$H$_4$Me), 2.460 (8) Å, and Cp$_3$Y·THF,[25] 2.451 (4) Å.

The iminoacyl ligand is η^2-bonded to the metal center and completes the pseudotetrahedral environment of the yttrium atom (Figure 1). The Y(1)–C(21) bond, 2.392 (3) Å, is shorter than those observed in the yttrium formimidoyl (Cp$_2$Y(η^2-CH=N-*t*-Bu))$_2$,[26] 2.545 (5) and 2.561 (5) Å, and is comparable with the Y–C distance in 1, 2.468 (7) Å, and in the anion (Cp$_2$Y(CH$_2$SiMe$_3$)$_2$)$^-$,[27] 2.402 (6) and 2.445 (6) Å. It is therefore obvious that the carbon atom C(21) is σ-bonded to yttrium. The Y(1)–N(1) distance is 2.407 (3) Å. This bond length is significantly longer than the known σ-YN bonds in Cp*$_2$YN(SiMe$_3$)$_2$,[2] 2.253 (5) and 2.274 (5) Å, and in (Cp$_2$Y(μ-N=CH-*t*-Bu))$_2$,[28] 2.314 (9) Å. In the latter complex the nitrogen atom bridges asymmetrically between two yttrium atoms, and the bond distance of this Y←N interaction is 2.382 (9) Å, which is comparable with the bond length in 11. Thus, in the complex under discussion here the YN bond represents a dative interaction.

Table VI. Selected Bond Angles (deg) for Cp*$_2$Y(η^2-C(DMB)=N(2,6-xylyl))•THF-d_8

O(1)–Y(1)–N(1)	80.2 (1)	N(1)–C(21)–C(22)	120.0 (3)
O(1)–Y(1)–C(21)	111.5 (1)	Y(1)–O(1)–C(39)	128.2 (2)
N(1)–Y(1)–C(21)	31.4 (1)	Y(1)–O(1)–C(42)	123.1 (2)
Y(1)–O(1)–C(31)	73.6 (2)	O(1)–C(39)–C(40)	106.7 (3)
Y(1)–C(21)–N(1)	161.7 (2)	O(1)–C(42)–C(41)	105.4 (4)
Y(1)–C(21)–C(22)	74.9 (2)	C(39)–C(40)–C(41)	105.6 (3)
C(21)–N(1)–C(31)	123.8 (3)	C(39)–O(1)–C(42)	102.1 (5)
C(21)–C(22)–C(23)	116.9 (3)		
Cp^0(1)–Y(1)–O(1)	102.6 (4)	Cp^0(1)–Y(1)–C(21)	103.3 (4)
Cp^0(2)–Y(1)–O(1)	99.8 (4)	Cp^0(2)–Y(1)–C(21)	101.9 (4)
Cp^0(1)–Y(1)–N(1)	113.6 (4)	Cp^0(1)–Y(1)–Cp^0(2)	132.0 (5)
Cp^0(2)–Y(1)–N(1)	111.7 (4)		

The C(21)–N(1) distance, 1.299 (4) Å, is a normal carbon–nitrogen double bond (1.30 Å[29]) and is comparable with the CN bond length observed in other η^2-iminoacyls: Ru(η^2-C(*p*-tolyl)=N(*p*-tolyl))Cl(CO)(PPh$_3$),[30] 1.30 (1) Å, (Cp$_2$Y(η^2-CH=N-*t*-Bu))$_2$,[26] 1.275 (6) Å, and Cp$_2$Ti(η^2-C-(Ph)=N(2,6-xylyl)),[21] 1.280 (6) Å. Thus, the double bond appears not to be affected by the η^2-coordination of the iminoacyl ligand to the metal.

The yttrium, O(1), and iminoacyl atoms N(1), C(21), C(22), and C(31) are in a plane (out of plane displacements are within 0.084 Å). The N(1)–Y(1)–C(21) and O(1)–Y(1)–N(1) angles are 31.4 (1) and 80.2 (1)° respectively. The bond angles N(1)–C(21)–C(22) of 120.0 (3)° and C(21)–N(1)–C(31) of 123.8 (3)° clearly indicate that the N(1) and C(21) atoms are sp^2-hybridized. This again shows that the C=N bond is not affected by η^2-coordination.

The 2,6-xylyl group (C(31)–C(38)) is twisted 62.5 (1)° out of the metal iminoacyl plane in order to diminish the steric interaction with the puckered THF ring. This ring is twisted 20.2 (2)° out of the same plane in the same direction. The methylene group (C(22)) of the DMB fragment is very favorable in minimizing the steric interaction between the two phenyl rings as these can freely bend away from each other.

The molecular structure of 11 irrefutably establishes the η^2-coordination of the iminoacyl ligand. It is reasonable to assume similar bonding in the iminoacyl complexes 9 and 10. This indicates that in d^0 metallocene iminoacyl complexes a $\nu_{C=N}$ between 1490 and 1550 cm^{-1} is indicative of η^2-coordination. For other iminoacyls IR absorptions in the same spectral region, but originating from well-established η^1-iminoacyl ligands, were reported (e.g. d^4 Mo complexes[20,31]). This makes clear one has to be very careful to correlate a particular bonding mode of an iminoacyl with absorptions in the IR spectrum. ^{13}C NMR

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(24) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008.

(25) Rogers, R. D.; Atwood, J. L.; Emad, A.; Sikora, P. J.; Rausch, M. D. *J. Organomet. Chem.* **1981**, *216*, 383.

(26) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 1252.

(27) Evans, W. J.; Dominguez, R.; Levan, K. R.; Doedens, R. J. *Organometallics* **1985**, *4*, 1836.

(28) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291.

(29) Sandorfy, C. In *The Chemistry of the Carbon-Nitrogen Double Bond*; Patai, S., Ed.; Interscience: London, 1970; p 2.

(30) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1978**, *157*, C27.

(31) Adams, R. A.; Chodosh, D. F. *Inorg. Chem.* **1978**, *17*, 41.

seems to be a more reliable technique.

Conclusions

The yttrium–carbon bond in 14-electron permethylyttrocenes Cp^*_2YR reacts readily with CX multiple bonds (X = =O, =S, N) provided that the substrate can coordinate to yttrium. In this respect the steric bulk of the carbyl R is very important. Too large a ligand may prevent an insertion reaction, either by inhibiting the formation of adducts $Cp^*_2YR{\cdot}S$ or by blocking the transition state for insertion. The insertion reactions presented above clearly demonstrate that a rich organometallic chemistry is accessible on the basis of carbyls Cp^*_2YR. The insertion products are in general 16-electron systems if the inserted substrate is a bidentate functionality. Even in these seemingly congested molecules space for additional ligands is available. This is convincingly demonstrated in the molecular structure of **11**, an η^2-iminoacyl THF adduct, it shows that in the organoyttrium systems under discussions the size of the coordination sphere is very large. It means that not only 18-electron systems are possible but also further, interesting reactions of the newly formed yttrium complexes may be anticipated.

Registry No. **1**, 95197-83-4; **2**, 108366-50-3; **3**, 108366-51-4; **4**, 108366-52-5; **5**, 108366-53-6; **6**, 108366-54-7; **7**, 108366-55-8; **8**, 108366-56-9; **9**, 108366-57-0; **10**, 108366-58-1; **11**, 108366-59-2; CO_2, 124-38-9; *t*-BuCN, 630-18-2; *t*-BuNC, 7188-38-7; CS_2, 75-15-0; (2,6-xylyl)NC, 2769-71-3.

Supplementary Material Available: Tables of atom coordinates, anisotropic thermal parameters, bond distances and (torsion) angles, and least-squares planes and atomic deviations therefrom, analysis of ring puckering, and analysis of the coordination or metal–metal geometry and ORTEP structure of $C_{42}H_{50}D_8NOY$ (**11**) showing the thermal ellipsoids (20 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Synthesis, Characterization, and Chemistry of Titanium(IV), Titanium(III), Zirconium(IV), and Hafnium(IV) Complexes of Phosphine Sulfides and Selenides. The Crystal and Molecular Structures of $Cp_2Ti(SPCy_2)_2$, $Cp_2Ti(S_2PCy_2)$, and $Cp_2Ti(Se_2PPh_2)$

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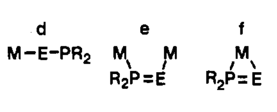
The complexes $Cp_2M(SPR_2)_2$ (M = Ti, R = Cy (**1**); M = Zr, R = Ph (**2**), R = Cy (**3**); M = Hf, R = Ph (**4**), R = Cy (**5**)) were prepared by reaction of $LiSPR_2$ with the appropriate metallocene dihalide. **1** crystallizes in the triclinic space group $P\bar{1}$, with a = 7.999 (2) Å, b = 13.102 (5) Å, c = 16.626 (6) Å, α = 96.71 (3)°, β = 101.43 (3)°, γ = 91.14 (3)°, V = 1694 (1) Å^3, and Z = 2. Species **2**–**5** could also be prepared from the reaction of $Cp_2M(PR_2)_2$ (M = Zr, Hf) with elemental sulfur. Reactions of Cp_2TiCl_2 with $LiXPR_2$ (X = S, R = Ph; X = Se, R = Ph, Cy) or solutions of **1** on standing yield Ti(III) species by reductive elimination of $(XPR_2)_2$. These Ti(III) complexes are formulated as "Cp_2TiXPR_2" (X = S, R = Ph (**6**), Cy (**7**); X = Se, R = Ph (**8**), R = Cy (**9**)) on the basis of EPR data. These Ti(III) compounds are unstable and slowly convert by chalcogen atom abstraction to the complexes $Cp_2TiX_2PR_2$ (X = S, R = Ph (**12**), R = Cy (**13**); X = Se, R = Ph (**14**), R = Cy (**15**)). **13** crystallizes in the orthorhombic space group *Pbna*, with a = 9.075 (3) Å, b = 34.052 (5) Å, c = 14.318 (5) Å, V = 4424 (3) Å^3, and Z = 8. **14** crystallizes in the monoclinic space group $P2_1/c$, with a = 8.471 (3) Å, b = 29.868 (9) Å, c = 8.336 (3) Å, β = 104.47 (3)°, V = 2030 (1) Å^3, and Z = 4. **12**–**15** as well as the analogues (X = S, R = Me (**10**), R = Et (**11**)) can also be prepared by photolysis of $Cp_2Ti(CO)_2$ in the presence of $(SPR_2)_2$ or XPR_2H. Alternatively, **12**–**15** can be prepared by reaction of either $LiXPR_2$ or LiX_2PR_2 with $[Cp_2TiCl]_2$. Complexes **2**–**5** slowly convert to the complexes $[Cp_2MX]_2$ (M = Zr, X = S (**16**), X = Se (**17**); M = Hf, X = S (**18**), X = Se (**19**), respectively). The preparation of **16**–**19** can also be achieved by direct reaction of **2**–**5** with $Cp_2M(PR_2)_2$. The differences between the Ti chemistry and that of Zr and Hf are attributed to the ease of reduction of Ti(IV) to Ti(III).

Introduction

Over the past several years, interest in early–late heterobimetallics has led us to develop several synthetic routes to such complexes. The methods we have devised are based on the use of early-transition-metal metalloligands as synthons.[1-7] In efforts to expand the arsenal of metalloligands available for heterobimetallic complex synthesis, we have investigated reactions of early transition metals with secondary phosphine chalcogenides. The high affinity of early metals for chalcogenide atom donors and

Chart I. Coordination Modes of Secondary Phosphine Chalcogenides and Their Conjugate Bases



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(1) White, G. S.; Stephan, D. W. *Inorg. Chem.* **1985**, *24*, 1499.

(2) Gelmini, L.; Matassa, L. C.; Stephan, D. W. *Inorg. Chem.* **1985**, *24*, 2585.

(3) Gelmini, L.; Stephan, D. W. *Inorg. Chim. Acta* **1986**, *111*, L17.

(4) Gelmini, L.; Stephan, D. W. *Inorg. Chem.* **1986**, *25*, 1222.

(5) Loeb, S. J.; Taylor, H. A.; Gelmini, L.; Stephan, D. W. *Inorg. Chem.* **1986**, *25*, 1977.

(6) Wark, T. A.; Stephan, D. W. *Inorg. Chem.* **1987** *26*, 363.

(7) White, G. S.; Stephan, D. W., unpublished results.

0276-7333/87/2306-1515$01.50/0