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Synthesis and Reactivity of Tervalent Paramagnetic Titanium Compounds $(\eta^5\text{-}C_5Me_5)_2TiR$: Molecular Structure of $(\eta^5\text{-}C_5Me_5)_2TiCH_2CMe_3$

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Paramagnetic, tervalent titanium compounds Cp^*_2TiR with R = Me (2), Et (3), *n*-Pr (4), CH_2CMe_3 (5), CH_2Ph (6), $\eta^3\text{-}C_3H_5$ (7), $\eta^3\text{-}C_4H_7$ (8), $CH{=}CH_2$ (9), $C{\equiv}CMe$ (10), Ph (11) have been prepared by salt metathesis from Cp^*_2TiCl (1).[1] The ^1H NMR spectra show characteristic broad resonances (width at half-maximum between 0.88 and 5.5 kHz) in the range δ 14.5–20.9 ppm, which are due to the ^1H nuclei of the Cp* ligands. Only part of the ^1H resonances of the carbyl ligand R are observed. ^2H NMR spectra of Cp^*_2TiR with deuterated ligands R allow assignment of all ^2H nuclei in R. These are observed between δ −79 and 125 ppm. Solution EPR spectra show broad singlet signals in the range $g = 1.941\text{–}1.992$, without hyperfine interaction with ^1H nuclei of the ligands or titanium isotope splitting. The crystal structure of 5 was determined by a single-crystal X-ray diffraction study. The compound crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. The cell dimensions are $a = 10.221$ (2) Å, $b = 15.609$ (3) Å, $c = 14.107$ (3) Å, and $\beta = 94.21$ (2)°. The refinements converged at $R(F) = 0.059$ for 2801 observed reflections and 359 parameters. Thermolysis of the compounds leads to quantitative formation of RH and a (pentamethylcyclopentadienyl)(fulvene)titanium compound, Cp*FvTi (Fv = $\eta^6\text{-}C_5Me_4CH_2$). The 15-electron compounds Cp^*_2TiR do not form stable adducts $Cp^*_2TiR{\cdot}L$, although intermediate adduct formation is indicated in reactions with substrates such as CO and isonitriles. With CO a complicated reaction occurs in which disproportionation to Ti(II) and Ti(IV), acyl formation, and nucleophilic attack on the Cp* ligand with ring expansion takes place. With isonitriles $RN{\equiv}C$ insertion in the Ti—R bond leads to formation of η^2-iminoacyls. Carbon dioxide reacts to give carboxylates $Cp^*_2Ti(\eta^2\text{-}O_2CR)$. For alkyls Cp^*_2TiR, where R bears a β-hydrogen, the dominant process is β-H transfer to an incoming substrate molecule and extrusion of the olefin R(−H). This has been observed for 3 and 4 with carbon dioxide, olefins, and but-2-yne.

Introduction

The paramagnetic, tervalent titanium compounds Cp^*_2TiR are rapidly becoming a very interesting class of compounds, not in the least because of their structural similarity to analogous d^0 group 3 metal and lanthanide complexes Cp^*_2MR, which are excellent catalysts for olefin hydrogenation, oligomerization, polymerization, and alkyne (cyclo)dimerization.[1,2] The selectivity of these catalysts seems to be strongly related to the size of the metal rather than to electronic differences. In the series Cp^*_2MR, titanium is the smallest metal and represents a steric extreme. Therefore, it is interesting to compare the reactivity of these titanium compounds with those of other metals. The 15-electron, d^1 compounds are not isoelectronic with their group 3 and lanthanide congeners, but the basic prerequisite for catalytic activity, viz. a free coordination site at the metal, is still fulfilled so that the titanium compounds Cp^*_2TiR are expected to show activity in olefin and alkyne hydrogenation and insertion chemistry. Furthermore, there is an obvious relation with tetravalent, cationic, 14-electron, d^0 titanium complexes $[Cp^*_2TiR]^+$ and the corresponding zirconium and hafnium compounds which have been studied extensively over the last years and have been shown to possess extremely interesting stoichiometric and catalytic reactivity.[3,4] Earlier work in our group explored the reactivity of the Ti–C bond in related cyclopentadienyl derivatives Cp_2TiR.[5] Many of these have a low thermal stability, but this could be improved simply by increasing the bulk of the ligand R. Reactivity of the compounds was then decreased, however. For small R studies were performed on compounds generated in situ, while for bulky ligands R the compounds generally were inert to substrate molecules (e.g. N_2). Exchanging the cyclopentadienyl for pentamethylcyclopentadienyl ligands also dramatically improves thermal stability of the titanium hydrocarbyls and allows us to study the reactivity of the smaller ligands R. Some aspects of the reactivity of these new compounds have been communicated earlier.[3b,6,7] Here we present a full account of the synthesis and characterization (including IR, EPR, and

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(1) The following abbreviations are used: Cp* = $\eta^5\text{-}C_5Me_5$, Cp = $\eta^5\text{-}C_5H_5$, R = carbyl ligand, Fv = $\eta^6\text{-}C_5Me_4CH_2$.

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$^1H/^2H$ NMR spectroscopy) of complexes Cp^*_2TiR, together with structural data and some exploratory results on their reactivity.

Experimental Section

General Considerations. All experiments were carried out under nitrogen or argon with use of Schlenk lines and gloveboxes or on a vacuum line equipped with a Töpler pump.[8] Solvents (pentane, Et_2O, THF, benzene, benzene-d_6, toluene-d_8) were purified by distillation from Na/K alloy. Cp^*_2TiCl (1) was made from $TiCl_2{\cdot}3THF$ and $Cp^*MgCl{\cdot}THF$ as described earlier.[6a] Grignard reagents (RMgX) and organolithium compounds (RLi) were made from the metals and the appropriate organic halides (Janssen, Merck) by following standard procedures. Benzylpotassium, $PhCH_2K$, was obtained by metalation of toluene with *t*-BuOK and *n*-BuLi[9] and MeC≡CLi from MeC≡CH and *n*-BuLi in THF at −30 °C. The deuterated Grignards (Et-d_5)MgBr and (Me-d_3)MgI were made from (Et-d_5)Br and (Me-d_3)I, respectively. (Pr-d_7)MgBr was prepared from (Pr-d_7)Br, made from (Pr-d_8)OD and PBr_3. Gaseous reagents CO (Matheson), MeC≡CH (Matheson), MeCl (Matheson), H_2 (Hoek-Loos, 99.9995%), and D_2 (Matheson) were used as purchased. Carbon dioxide was made by oxidation of CO over CuO at 320 °C on a vacuum line. Other reagents (nitriles, isonitriles) were purified by conventional techniques and dried over activated 4-Å molecular sieves.

NMR spectra were recorded on Bruker WH-90DS and Varian VXR-300 FT spectrometers. Chemical shifts are given in ppm, downfield from TMS (δ 0.00, ^1H, ^{13}C) or TMS-d_{12} (δ 0.00, ^2H) as positive and are referenced to residual protons/deuterons in the solvents (benzene, δ = 7.15 ppm; toluene, δ = 6.98 ppm). EPR spectra were recorded on a Varian E4 spectrometer with DPPH (g = 2.0037) as external reference and IR spectra on a Pye-Unicam SP3-300 spectrophotometer from Nujol mulls between KBr disks. UV–vis spectra were recorded on a Perkin-Elmer EPS-3T spectrophotometer. GC analyses were performed on a HP 7620A instrument using a Porapak Q packed column or on a Packard 428 instrument using a 50-m, 0.2-mm inside diameter CpSil 5CB capillary column. Electron impact mass spectra were measured with an AEI MS-902 instrument operating at 70 eV (unless stated otherwise). GC–MS analyses were obtained by Dr. A. P. Bruins on a Finnegan 3300 instrument using a 25-m, 0.5-mm inside diameter CpSil 5CB capillary column. Molecular weights were determined by cryoscopy in benzene solutions with use of an instrument built according to ref 10. Elemental analyses were performed at the Analytical Center of this department. Given values are the average of at least two independent determinations.

Preparation of $CD_2CDMgBr$. $CD_2CDMgBr$ was prepared from 1,2-dibromoethane-d_4 (Akademie der Wissenschaften der DDR) as follows. To a stirred solution of 5 g of KOH in 30 mL of water and 50 mL of ethanol was added 20 g of $C_2D_4Br_2$ at 50 °C. The formed vinyl bromide was distilled over a Widmer column and collected in a cold trap containing 40 mL of THF. After 2 h collection was stopped, and 1.2 g of Mg was added to the THF solution. The mixture soon started to reflux, and after 3 h reaction was complete, yielding a 0.32 M $CD_2CDMgBr$ solution.

Preparation of (Ph-d_5)Na·NaCl. (Ph-d_5)Na·NaCl was prepared from 677 mg of Na (29.4 mmol) and 1.60 mL of PhCl-d_5 (15.7 mmol); Aldrich) in 50 mL of pentane. The mixture was refluxed for 4 h, and after evaporation of the solvents the black precipitate was isolated.

Cp^*_2TiMe (2). A solution of 14.6 g (41.6 mmol) of 1 in 200 mL of Et_2O was cooled to −80 °C, and 30.4 mL of 1.36 M MeMgI (41.3 mmol) in Et_2O was syringed in. Reaction took place immediately, and the color changed from blue to green. The mixture was warmed to room temperature in 2 h, and the solvent was then removed under vacuum. The residue was extracted with pentane and the extract concentrated to about 60 mL and then cooled to −80 °C. A first crop of green crystals was isolated. Concentrating the mother liquor and cooling gave more product; total yield 12.1 g (36.4 mmol, 88%) of green crystals of 2. Recrystallization from pentane gave analytically pure 2. Anal. Calcd for $C_{21}H_{33}Ti$: C, 75.66; H, 9.98; Ti, 14.37; mol wt, 333. Found: C, 75.47; H, 10.00; Ti, 14.48; mol wt (C_6H_6), 333 ± 30. IR (cm^{-1}): 2720 (m), 1490 (s), 1435 (s), 1385 (vs), 1165 (w), 1110 (m), 1065 (m), 1025 (s), 960 (w), 805 (m), 660 (m), 600 (w), 560 (w), 440 (s), 400 (w).

$Cp^*_2TiCD_3$ (2-d_3). Compound 2-d_3 was prepared in a way similar to that for 2, from 1 (1.21 g, 3.42 mmol) and CD_3MgI (3.43 mmol); yield 0.93 g (2.78 mmol, 81%).

Cp^*_2TiEt (3). In a procedure similar to the one followed for 2, compound 3 was obtained from 10.2 g (28.9 mmol) of 1 and 29 mmol of EtMgBr in Et_2O; total yield 8.7 g (25.1 mmol, 87%) of brown crystals. Anal. Calcd for $C_{22}H_{35}Ti$: C, 76.06; H, 10.15; Ti, 13.79; mol wt (C_6H_6), 347. Found: C, 75.41; H, 10.09; Ti, 13.64; mol wt, 341 ± 30. IR (cm^{-1}): 2720 (m), 2390 (w), 2340 (w), 1485 (m), 1435 (s), 1370 (vs), 1160 (w), 1125 (w), 1090 (w), 1075 (w), 1065 (m), 1025 (s), 980 (w), 860 (m), 800 (m), 635 (m), 475 (m), 415 (s).

$Cp^*_2TiC_2D_5$ (3-d_5). Compound 3-d_5 was obtained analogously to 3, from 1 (2.93 g, 8.3 mmol) and C_2D_5MgBr (8.3 mmol) in Et_2O at −80 °C; yield 2.36 g (6.7 mmol, 80%).

Cp^*_2Ti-*n*-Pr (4). A solution of 2.60 g (7.6 mmol) of 1 in 100 mL of Et_2O was stirred at −80 °C. *n*-PrMgBr (7.6 mmol) in Et_2O was added dropwise over 0.5 h. The blue solution turned dark green. After the mixture was stirred at −30 °C for 2 h, the solvent was removed under vacuum (−30 °C). The residue was extracted with pentane at −20 °C. The extracts were concentrated to about 30 mL and cooled to −80 °C. Green crystals separated and were isolated after washing with cold pentane and drying under vacuum at −20 °C; yield 1.7 g (4.7 mmol, 62%). Anal. Calcd for $C_{23}H_{37}Ti$: C, 76.43; H, 10.32; Ti, 13.25; mol wt, 361. Found: C, 75.69; H, 9.93; Ti, 13.53; mol wt (C_6H_6), 340 ± 30. IR (cm^{-1}): 2720 (m), 1490 (m), 1380 (vs), 1300 (m), 1260 (w), 1170 (w), 1150 (w), 1120 (m), 1065 (m), 1025 (s), 800 (m), 725 (m), 620 (w), 565 (w), 515 (m), 425 (m). Compound 4 is thermally unstable and decomposes slowly in the solid state even when stored at −35 °C.

Cp^*_2Ti-*n*-C_3D_7 (4-d_7). Compound 4-d_7 was made analogously to 4 by starting from 0.64 g (4.64 mmol) of 1 and 13 mL of a 0.36 M solution of (Pr-d_7)MgBr in ether; yield 0.51 g (1.39 mmol, 30%).

$Cp^*_2TiCH_2CMe_3$ (5). To a solution of 0.61 g (1.72 mmol) of 1 in 25 mL of Et_2O, was added 1.72 mmol of $LiCH_2CMe_3$ in 7 mL of Et_2O at −30 °C. The blue solution turned brown-green. The mixture was warmed to room temperature and stirred for 1 h. The solvent was removed under vacuum and the residue extracted with pentane. The extract was concentrated to 10 mL and cooled to −80 °C. Brown-green crystals formed, which were filtered off, washed with cold pentane, dried under vacuum, and isolated; yield 0.50 g (1.28 mmol, 74%). Anal. Calcd for $C_{25}H_{41}Ti$: C, 77.09; H, 10.61; Ti, 12.30; mol wt, 389. Found: C, 77.36; H, 10.68; Ti, 11.54; mol wt (C_6H_6), 400 ± 25. IR (cm^{-1}): 2705 (w), 2695 (vw), 1485 (m), 1455 (s, br), 1375 (s), 1350 (s), 1250 (w), 1215 (m), 1195 (m), 1160 (w), 1095 (w), 1060 (w), 1020 (s), 985 (w), 945 (w), 915 (w), 895 (w), 800 (w), 735 (m), 615 (w), 575 (m), 550 (w), 495 (w).

$Cp^*_2TiCH_2Ph$ (6). Benzene (20 mL) was added to a mixture of 1.54 g (4.35 mol) of 1 and 0.57 g (4.35 mmol) of KCH_2Ph. Reaction started immediately, and a brown mixture formed. After the mixture was stirred for 1 h at room temperature, the solvent was removed under vacuum. The residue was extracted with pentane. The extract was concentrated to 10 mL and then slowly cooled to −80 °C. Brown crystals separated, which were isolated; yield 1.35 g (3.29 mmol, 76%). Anal. Calcd for $C_{27}H_{37}Ti$: C, 79.19; H, 9.11. Found: C, 79.30; H, 9.22. IR (cm^{-1}): 3040 (m), 2720 (w), 1910 (w), 1840 (w), 1785 (w), 1595 (s), 1480 (s), 1440 (s), 1375 (vs), 1270 (w), 1195 (s), 1095 (w), 1050 (m), 1020 (s), 985 (m), 965 (w), 885 (w), 840 (w), 800 (s), 750 (vs), 710 (s), 590 (m), 550 (m), 510 (m), 420 (m).

$Cp^*_2Ti(\eta^3\text{-}C_3H_5)$ (7). A solution of 5.95 g (16.8 mmol) of 1 in 100 mL of Et_2O was stirred at −80 °C, and 16.8 mL of a 1.0 M solution of C_3H_5MgBr in Et_2O was added dropwise. The mixture was warmed to room temperature and then stirred for 2 h. The color changed from blue to dark green. The solvent was pumped off and the residue extracted with pentane. The extract was concentrated to 25 mL and then slowly cooled to −80 °C. The dark green crystals that separated were filtered off, washed with

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cold pentane, dried under vacuum, and isolated; yield 2.15 g (6.0 mmol, 36%). Anal. Calcd for $C_{23}H_{35}Ti$: C, 76.86; H, 9.82; Ti, 13.33; mol wt, 359. Found: C, 76.42; H, 9.85; Ti, 13.31; mol wt (C_6H_6), 360 ± 30. IR (cm^{-1}): 3110 (w), 2710 (m), 1615 (w), 1565 (w), 1505 (s), 1490 (m), 1440 (s), 1380 (vs), 1255 (m), 1215 (m), 1160 (w), 1095 (w), 1060 (w), 1025 (s), 910 (w), 805 (vs), 750 (s), 650 (m), 625 (w), 470 (w), 430 (w).

$Cp^*_2Ti(\eta^3\text{-}C_4H_7)$ (8). The procedure for 8 was analogous to that for 7. From 2.0 g (5.7 mmol) of 1 and an equivalent amount of (1-methylallyl)MgBr was obtained 1.0 g (2.7 mmol) of 8 as black crystals. Anal. Calcd for $C_{24}H_{37}Ti$: C, 77.19; H, 9.99; Ti, 12.83; mol wt, 373. Found: C, 76.73; H, 9.92; Ti, 12.63; mol wt (C_6H_6), 341 ± 30. IR (cm^{-1}): 3080 (w), 2270 (w), 1540 (m), 1480 (m), 1380 (s), 1280 (w), 1190 (m), 1160 (m), 1110 (w), 1060 (w), 1020 (m), 995 (w), 975 (w), 880 (w), 810 (m), 740 (m), 650 (m), 615 (w), 520 (w), 430 (w).

$Cp^*_2TiCHCH_2$ (9). A suspension of 3.40 g (9.6 mmol) of 1 in 20 mL of pentane was mixed with 9.6 mmol of $CH_2CHMgCl$ in THF at room temperature. The mixture was stirred overnight. The volatiles were removed in vacuo, and the green residue was extracted with pentane. The extract was concentrated and cooled to −80 °C. Dark green crystals separated; yield 2.81 g (8.14 mmol, 85%). Anal. Calcd for $C_{22}H_{33}Ti$: C, 76.50; H, 9.63; Ti, 13.87. Found: C, 76.29; H, 9.67; Ti, 13.66. IR (cm^{-1}): 2720 (w), 1780 (w), 1550 (w), 1380 (vs), 1220 (m), 1160 (m), 1065 (w), 1020 (s), 890 (s), 800 (w), 590 (w), 570 (w), 550 (w), 485 (s), 435 (m).

$Cp^*_2TiCDCD_2$ (9-d_3). Compound 9-d_3 was prepared analogously to 9 by starting from 1.21 g (3.41 mmol) of 1 and 11.7 mL of a 0.32 M solution of $CD_2CDMgBr$ in THF; yield 0.791 g (2.27 mmol, 66%).

$Cp^*_2TiCCMe$ (10). A mixture of 0.79 g (2.24 mmol) of 1 and 0.103 g (2.24 mmol) of MeCCLi in 20 mL of THF was stirred at room temperature for 24 h. The solvent was removed under vacuum and the residue extracted with pentane. The extract was concentrated to 10 mL and cooled to −80 °C. Green microcrystalline product was obtained; yield 0.45 g (1.26 mmol, 56%). Anal. Calcd for $C_{23}H_{33}Ti$: C, 77.29; H, 9.31; Ti, 13.40. Found: C, 76.25; H, 9.35; Ti, 13.47. IR (cm^{-1}): 3670 (w), 2720 (w), 2080 (w), 1480 (m), 1380 (vs), 1365 (m), 1165 (w), 1145 (w), 1060 (w), 1025 (s), 970 (m), 800 (w), 610 (w), 580 (m), 450 (s), 400 (m).

Cp^*_2TiPh (11). A mixture of 17.8 g (50.2 mmol) of 1 and 55 mmol of PhMgBr in 200 mL of Et_2O was stirred for 24 h at room temperature. The color changed from blue to dark green. The solvent was removed under vacuum and the residue extracted with pentane. Concentration and cooling of the extracts to −80 °C gave several crops of dark green crystals, total yield 17.9 g (45.2 mmol, 90%). Analytically pure 11 was obtained by recrystallization from pentane. Anal. Calcd for $C_{26}H_{35}Ti$: C, 78.97; H, 8.92; Ti, 12.11; mol wt, 395. Found: C, 78.80; H, 8.83; Ti, 12.12; mol wt (C_6H_6), 390 ± 30. IR (cm^{-1}): 3120 (w), 3100 (w), 3040 (m), 2710 (w), 1555 (m), 1485 (m), 1420 (m), 1380 (vs), 1315 (w), 1240 (m), 1170 (m), 1065 (w), 1055 (w), 1025 (s), 995 (w), 980 (w), 900 (w), 860 (w), 810 (w), 730 (vs), 715 (vs), 680 (w), 630 (w), 620 (w), 555 (w), 480 (s), 440 (s), 410 (w).

$Cp^*_2Ti(Ph\text{-}d_5)$ (11-d_5). A mixture of 1.01 g (2.85 mmol) of 1 and 0.68 g of (Ph-d_5)Na·NaCl were suspended in 10 mL of pentane. The color changed to green, and after the mixture was stirred for 1 h, the solution was filtered off. Crystallization at −80 °C yielded 0.825 g (2.0 mmol, 72%).

Table I. Crystallographic Data for 5

chem formula	$C_{25}H_{41}Ti$	cryst size, mm	0.04 × 0.20 × 0.20
mol wt	389.48	$\omega/2\theta$ scan, deg	$\Delta\omega = 0.85 + 0.35 \tan\theta$
space group	$P2_1/n$	θ^{max}, deg	≤28.0
a, Å	10.221 (2)	data set	h, −13 to 0; k, 0–20; l, −18 to 18
b, Å	15.609 (3)	no. of data collected	5926
c, Å	14.107 (3)	no. of unique data	5419
β, deg	94.21 (3)	no. of rflns obsd ($I > 2.5\sigma(I)$)	2801
V, Å^3	2244.6 (8)	no. of params refined	359
Z	4	$R(F)$	0.059
D_{calcd}, g cm^{-3}	1.152	$R_w(F)$	0.066
$F(000)$, e	852	w	$1/\sigma^2(F)$
μ(Mo Kα), cm^{-1}	3.8	S	1.291
T, K	130		

Table II. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-H Atoms with Esd's in Parentheses

	x	y	z	U_{eq}, Å^{2a}
Ti(1)	0.20710 (7)	0.26193 (4)	0.44692 (5)	0.0101 (2)
C(1)	0.0248 (4)	0.2973 (3)	0.5428 (3)	0.016 (1)
C(2)	0.0152 (4)	0.3452 (3)	0.4569 (3)	0.015 (1)
C(3)	0.1188 (4)	0.4048 (2)	0.4605 (3)	0.017 (1)
C(4)	0.1991 (4)	0.3891 (3)	0.5445 (3)	0.018 (1)
C(5)	0.1397 (4)	0.3244 (3)	0.5958 (3)	0.019 (1)
C(6)	−0.0812 (4)	0.2429 (3)	0.5755 (3)	0.028 (2)
C(7)	−0.1012 (5)	0.3437 (3)	0.3872 (3)	0.032 (2)
C(8)	0.1209 (5)	0.4830 (3)	0.3993 (3)	0.030 (2)
C(9)	0.3122 (5)	0.4422 (3)	0.5825 (4)	0.035 (2)
C(10)	0.1833 (6)	0.3019 (3)	0.6965 (3)	0.033 (2)
C(11)	0.3638 (4)	0.3285 (3)	0.3480 (3)	0.018 (2)
C(12)	0.4217 (4)	0.2551 (3)	0.3901 (3)	0.018 (1)
C(13)	0.3532 (4)	0.1832 (2)	0.3522 (3)	0.015 (1)
C(14)	0.2470 (4)	0.2124 (3)	0.2908 (3)	0.014 (1)
C(15)	0.2545 (4)	0.3027 (3)	0.2867 (3)	0.018 (1)
C(16)	0.4263 (5)	0.4152 (3)	0.3541 (4)	0.031 (2)
C(17)	0.5472 (4)	0.2524 (3)	0.4518 (3)	0.029 (1)
C(18)	0.4003 (5)	0.0928 (3)	0.3557 (3)	0.027 (2)
C(19)	0.1510 (5)	0.1587 (3)	0.2337 (3)	0.027 (2)
C(20)	0.1750 (5)	0.3559 (3)	0.2157 (3)	0.027 (2)
C(21)	0.1574 (4)	0.1283 (3)	0.4874 (3)	0.015 (1)
C(22)	0.2159 (4)	0.0696 (3)	0.5693 (3)	0.020 (1)
C(23)	0.2242 (5)	−0.0232 (3)	0.5362 (3)	0.028 (2)
C(24)	0.3533 (4)	0.0985 (3)	0.6060 (3)	0.023 (1)
C(25)	0.1305 (5)	0.0700 (3)	0.6532 (3)	0.033 (2)

^{a} $U_{eq} = {}^1/_3 \sum_i \sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

X-ray Crystal Structure of 5. Suitable green, block-shaped crystals were grown from pentane. Data collection was done on an Enraf-Nonius CAD-4F diffractometer equipped with a low-temperature device. Lattice parameters were derived from the angular settings of 23 reflections in the range 6.34° < θ < 18.39°. The intensities of the data were corrected for scale variation, Lorentz, and polarization effects, but not for absorption. Crystal data and experimental details are given in Table I. The structure was solved by direct methods (Multan)[11] and Fourier techniques. Refinement was carried out by block-diagonal least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms.[12] Hydrogens located on a difference Fourier map were included in the final refinement with one overall temperature factor. A final difference Fourier map did not show any significant residual features. The reflections 10,8,9 and 4,11,14 with a $\Delta F/\sigma(F)$ ratio of 15.4 and 51.0, respectively, were excluded from the final refinement cycles. Final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table II. Neutral atom scattering factors[13] were used with anomalous dispersion corrections[14] being applied to the non-hydrogen atoms. All calculations were carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the packages XTAL,[12] and EUCLID[15] (calculation of geometric data).

Thermal Decomposition Studies. Samples were sealed in glass capillaries and heated slowly, while being observed under a microscope. Compounds **2–5**, **9**, and **11** decomposed without

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melting, whereas **6** melted with decomposition at about 75 °C. The allyls **7** and **8** showed regular melting points at 180 and 105 °C, respectively. These two and compound **10** could be heated up to 200 °C without notable decomposition. An impression of the relative stabilities was obtained from DTA measurements (5–10-mg samples in sealed ampules, heating rate 2–3 °C min^{-1}). Decomposition was indicated by exothermal effects. The following order was established: **4** (60 °C), **3** (70 °C), **6** (80 °C), **9** (85 °C), **2** (95 °C), **11** (150 °C). For **7**, **8**, and **10** no exothermal effect was observed below the maximum temperature reached (200 °C). In all cases thermal decomposition of Cp*$_2$TiR was indicated by formation of RH (GC) and a purple product, which was identified by spectroscopy (IR, ^{1}H, NMR, UV–vis) as Cp*FvTi (**12**; Fv = η^6-C$_5$Me$_4$CH$_2$).[16,17] The decomposition of **11** takes place at a temperature where **12** is not stable, so that thermolysis of **11** resulted in formation of benzene, **12**, and its decomposition products H$_2$ and Cp*[η^7-C$_5$Me$_3$(CH$_2$)$_2$]Ti (**13**).[17]

Thermolysis in Solution. In other common organic solvents (pentane, benzene, toluene, THF), compounds Cp*$_2$TiR decompose as in the solid state, giving quantitative yields of RH and **12**.

Thermolysis of Cp*$_2$TiMe (2) in Toluene. Preparative Scale. A solution of **2** (1.29 g, 3.87 mmol) in 25 mL of toluene was heated at 110 °C over 50 h. The color changed from green to purple. The solvent was removed under vacuum and the residue sublimed (100 °C, 10^{-3} Torr) to give purple, crystalline Cp*FvTi (**12**), yield 1.14 g (3.60 mmol, 93%). The product was identified by comparing the IR and ^{1}H NMR spectra with those of **12**.[16,17]

Töpler Pump Determination. A solution of **2** (0.118 g, 0.35 mmol) in 15 mL of toluene was heated at 105 °C for 10 h. The gas liberated was vacuum-transferred to a calibrated volume and measured; yield 0.34 mmol (0.96 mol per mol of Ti). It was shown by GC and MS that the gas was exclusively methane. The purple residue was identified spectroscopically as **12**.[16,17]

Ligand Exchange Reactions. Reactions were carried out in a two-compartment vessel under vacuum. A typical experiment is described below. Compound **3** (57 mg, 0.164 mmol) and 0.10 mL of a 1.61 M MeMgCl solution in THF were placed in separate compartments of the vessel and frozen in liquid nitrogen. THF (5 mL) was condensed into the vessel, and the compounds were mixed at −80 °C. After the mixture was stirred for 4 h at −80 °C, the evolved gases were collected in a calibrated volume (0.117 mmol, 71%) and analyzed with GC (methane). The residue was dried under vacuum and extracted with pentane. The extract was characterized by ^{1}H NMR spectroscopy: Cp*$_2$TiMe (30%); Cp*$_2$Ti(η^2-C$_2$H$_4$) (70%). Analysis of the pentane-insoluble gray residue gave a Mg:Cl ratio of 1:1.

Reaction with Carbon Monoxide. On a vacuum line, carbon monoxide (0.35 mmol) was admitted into a solution of 116 mg (0.35 mmol) of **2** in 3 mL of pentane at −80 °C. The solution turned dark blue on warming to 0 °C. The solvent was then removed under vacuum. The resulting purple-blue solid was identified as the acyl compound Cp*$_2$TiCOMe (**14**). IR (cm^{-1}): 2720 (w), 1530 (m), 1490 (w), 1455 (s), 1380 (vs), 1325 (m), 1110 (s), 1060 (w), 1025 (s), 950 (w), 800 (w), 555 (m), 440 (s). ^{1}H NMR (90 MHz, benzene-d_6, 22 °C): δ = 24.1 ppm (Cp*, 30 H, fwhm 1.8 kHz), δ = −0.9 ppm (Me, 3 H, fwhm 600 Hz).

A similar experiment with **3** afforded dark blue Cp*$_2$TiCOEt (**15**). IR (cm^{-1}): 2720 (w), 1520 (m), 1475 (w), 1445 (m), 1430 (m), 1370 (s), 1330 (w), 1310 (w), 1160 (w), 1110 (w), 1075 (s), 1020 (s), 920 (s), 815 (w), 690 (w), 660 (w), 610 (w), 435 (w). ^{1}H NMR (90 MHz, benzene-d_6, 22 °C): δ = 23.8 ppm (Cp*, 30 H, fwhm 2100 Hz), δ = 0.91 ppm (Et, 5 H, fwhm 50 Hz). Both acyl compounds decompose within a few hours when kept at room temperature.

Reaction of 2 with Me$_3$CN≡C. Me$_3$CN≡C (200 μL) was added by syringe to a solution of 483 mg (1.45 mmol) of **2** in 10 mL of pentane. The mixture was stirred at room temperature for 0.5 h, while the solution turned blue. The solvent and other volatiles were removed under vacuum. The gray residue was crystallized from pentane at −80 °C; yield 101 mg (0.242 mmol, 17%) of gray-blue crystals of Cp*$_2$TiC(Me)=NCMe$_3$ (**16**). Anal. Calcd for C$_{26}$H$_{42}$NTi: C, 74.94; H, 10.16; Ti, 11.50; N, 3.36. Found: C, 74.52; H, 9.93; Ti, 11.48; N, 3.35. IR (cm^{-1}): 2710 (w), 1600 (s), 1220 (m), 1200 (m), 1180 (s), 1070 (m), 1020 (s), 790 (w), 620 (w), 540 (w), 420 (w). ^{1}H NMR (300 MHz, benzene-d_6, 20 °C): δ = 20.3 ppm (Cp*, 30 H, fwhm 5.50 kHz), δ −0.2 ppm (*t*-Bu, 9 H, fwhm 125 Hz), δ = 1.7 ppm (Me, 3 H, fwhm 11 Hz).

Reaction of 2 with Carbon Dioxide: Preparation of Cp*$_2$Ti(η^2-O$_2$CMe) (17a). A solution of 0.79 g (2.40 mmol) of **2** in 20 mL of Et$_2$O was cooled to −196 °C, and an excess of CO$_2$ was condensed in. During warming to room temperature the color changed to light blue. Excess CO$_2$ and the solvent were removed. The residue was crystallized from 10 mL of Et$_2$O; yield 0.64 g (1.70 mmol, 71%) of **17a**. Anal. Calcd for C$_{22}$H$_{33}$O$_2$Ti: C, 70.02; H, 8.81; Ti, 12.69. Found: C, 69.88; H, 8.84; Ti, 12.63. IR (cm^{-1}): 2710 (w), 2395 (w), 1610 (w), 1530 (s, ν_{asym}(OCO)), 1480 (m), 1455 (vs, ν_{sym}(OCO)), 1375 (s), 1230 (w), 1155 (w), 1120 (w), 1060 (w), 1020 (w), 935 (s), 795 (w), 680 (s), 620 (m), 545 (s), 415 (s), 375 (m). ^{1}H NMR (C$_6$D$_6$): δ = 15.5 ppm (Cp*, 30 H, fwhm 5.00 kHz), δ = −1.20 ppm (Me, 3 H, fwhm 500 Hz).

Reaction of Other Compounds with Carbon Dioxide. In reactions similar to the one described above, compounds **5**–**7** and **9**–**11** were allowed to react with CO$_2$. Compound **11** did not react at room temperature within 150 h. The others reacted within 24 h to give blue carboxylates, Cp*$_2$Ti(η^2-O$_2$CR) (**17b**–**f**). Identification was made from their IR and ^{1}H NMR spectra. The data are given as supplementary material.

Reaction of 3 and 4 with Carbon Dioxide. Töpler Pump Experiments. **3** (0.089 g, 0.26 mmol) in 2 mL of toluene was stirred at −80 °C and connected to a bulb with 0.26 mmol of CO$_2$. During warming to room temperature the color of the solution changed from brown to blue. The gas produced was pumped off and analyzed by GC and MS: found 0.24 mmol (0.96 mol per mol of Ti) of ethene. The blue solid residue was identified as the formate Cp*$_2$Ti(η^2-O$_2$CH) (comparison of ^{1}H NMR and IR spectra with those of an authentic sample[6a]). A similar reaction with **4** (0.081 mmol) gave exclusively propene (0.084 mmol; GC, MS) and Cp*$_2$Ti(η^2-O$_2$CH) (**17g**). Traces of ethane (propane for **4**) were also found, presumably due to thermolysis of the alkyls.

Preparative Scale. A solution of 0.200 g (0.554 mmol) of **4** in 20 mL of Et$_2$O was cooled to −196 °C, and 0.68 mmol of CO$_2$ was condensed in. When it was warmed to room temperature, the mixture turned blue-green. The solvent was pumped off and the residue crystallized from pentane to give 0.156 g (0.43 mmol, 78%) of blue Cp*$_2$Ti(η^2-O$_2$CH) (**17g**).

Reaction of 2 with But-2-yne. A solution of 241 mg (0.72 mmol) of **2** in 2 mL of but-2-yne was stirred at room temperature for 48 h. The excess of but-2-yne was pumped off under vacuum, and the green residue was crystallized (−80 °C) from 2 mL of pentane; yield 107 mg (0.28 mmol, 40%) of green crystals of Cp*$_2$TiC(Me)=CMe$_2$ (**9a**). Anal. Calcd for C$_{25}$H$_{39}$Ti: C, 77.49; H, 10.14; Ti, 12.36. Found: C, 77.25; H, 10.15: Ti, 12.46. IR (cm^{-1}): 2710 (w), 1260 (w), 1200 (w), 1160 (w), 1090 (m), 1060 (w), 1020 (s), 435 (s). ^{1}H NMR (90 MHz, benzene-d_6, 22 °C): δ = 17.9 (Cp* + Me, 33 H, fwhm 2.0 kHz), δ = 5.88 (Me, 3 H, fwhm 160 Hz). An analogous procedure was used to prepare **9a**-d_3, Cp*$_2$TiC(Me)=C(Me)(Me-d_3), by starting from **2**-d_3.

Reaction of 3 with But-2-yne. To a solution of 60 mg (0.172 mmol) of **3** in 2 mL of toluene was added (vacuum line) 0.17 mmol of but-2-yne. The mixture was stirred at room temperature while it slowly turned green. After 1.5 h, 0.17 mmol of gas was pumped off and identified as exclusively ethene (GC). The toluene was removed under vacuum and the green residue identified as Cp*$_2$TiC(Me)=C(H)Me (**9b**) by IR and ^{1}H NMR spectroscopy and reaction with HCl. Anal. Calcd for C$_{24}$H$_{37}$Ti: C, 77.20; H, 9.99; Ti, 12.83. Found: C, 76.65; H, 9.86; Ti, 12.45. IR (cm^{-1}): 2720 (w), 1260 (w), 1160 (w), 1140 (w), 1060 (w), 1020 (s), 800 (m), 580 (m), 420 (m). ^{1}H NMR (90 MHz, benzene-d_6, 22 °C): δ = 15.4 (Cp*, fwhm 14 kHz).

Reaction of **9b** with HCl (toluene, −80 °C) gave Cp*$_2$TiCl (**1**: IR, ^{1}H NMR) and *cis*-2-butene (GC) in a 1:1 ratio.

Reaction of 2 with Acetone: Preparation of the Adduct Cp*$_2$TiMe(O=CMe$_2$). Cp*$_2$TiMe (422 mg, 1.27 mmol) was dissolved in 10 mL of pentane. Acetone (93 μL, 1.27 mmol) was added at room temperature. No color change was observed. After it was stirred for 3 h, the solution was concentrated and cooled to −80 °C. Brownish green crystals precipitated; yield 102 mg

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(0.26 mmol, 21%). IR (cm^{-1}): 2720 (w), 1620 (m), 1280 (s), 1150 (b), 1040 (m), 1020 (s), 950 (w), 870 (w), 800 (w), 770 (w), 440 (w), 370 (w). In solution the adduct dissociates into **2** and acetone. Due to the broad resonances no reliable ^{1}H NMR data could be obtained.

Results and Discussion

Synthesis. The readily available Cp^*_2TiCl (**1**)[6a] is a convenient starting material for a wide range of titanium hydrocarbyl derivatives Cp^*_2TiR, by use of salt metathesis (eq 1). All reactions proceed smoothly at or below room temperature (in Et_2O or THF), leading to essentially quantitative formation of Cp^*_2TiR.

$$\underset{\mathbf{1}}{Cp^*_2TiCl} + RM \rightarrow \underset{\mathbf{2-11}}{Cp^*_2TiR} + MCl \qquad (1)$$

M = Li, K, MgX; R = Me (**2**), Et (**3**), *n*-Pr (**4**), CH_2CMe_3 (**5**), CH_2Ph (**6**), η^3-C_3H_5 (**7**), η^3-C_4H_7 (**8**), $CH{=}CH_2$ (**9**), $C{\equiv}CMe$ (**10**), Ph (**11**)

The thermal stability of **3** and **4** (vide infra) makes it difficult to obtain these compounds analytically pure. Low thermal stability of the products frustrated attempts to obtain Cp^*_2TiR with higher primary (except for CH_2CMe_3), secondary, or tertiary alkyl ligands. Normally, only the thermal decomposition product Cp*FvTi (Fv = η^6-$C_5Me_4CH_2$)[16,17] could be isolated in these cases. Grignard reagents with extremely bulky groups, e.g. $2\text{-}MeC_6H_4MgBr$ or $2,6\text{-}Me_2C_6H_3MgBr$, did not react with **1** or Cp^*_2TiBr, even when the reaction mixtures were refluxed for 7 days in THF. This is in clear contrast with the Cp_2Ti system, where introduction of these bulky ligands under ambient conditions is quite easy.[5,18] The bulk of the pentamethylcyclopentadienyl ligands appears to cause this dramatic decrease in reaction rate. An interesting alternative route to higher alkyl compounds Cp^*_2TiR is through α-olefin insertion into the Ti–H bond of Cp^*_2TiH (eq 2).

$$\underset{\mathbf{14}}{Cp^*_2TiH} + CH_2{=}CHR \rightarrow \underset{\begin{subarray}{l}\mathbf{3}\ (R = H)\\ \mathbf{4}\ (R = Me)\end{subarray}}{Cp^*_2TiCH_2CH_2R} \qquad (2)$$

The method is mentioned here as a convenient way of in situ preparation of pure thermolabile alkyls. It is limited to α-alkenes. Internal olefins exhibit significantly lower insertion rates and yield primary alkyl products as well. Details of the method will be described elsewhere.[19]

Binding of magnesium or alkali-metal salts and solvent molecules, as is frequently encountered with other group 4 elements[20] and as is normal for group 3 metal and lanthanide complexes Cp^*_2MR,[21] is not observed in our system. We assume that although compounds Cp^*_2TiR are 15-electron systems and thus electron deficient, the diminished Lewis acidity of the titanium center and the presence of an additional electron make complexation of salt or solvent molecules thermodynamically unfavorable.

Characterization. General Comments. The pure compounds Cp^*_2TiR (**2–11**) are crystalline, extremely air-sensitive compounds. The alkyls **2**, **4**, and **5** are green; the ethyl **3** is brown. The benzyl **6** is dark brown, the allyls are green (**7**) or purple (**8**), and the vinyl **9**, the alkynyl **10**, and the phenyl **11** are green. The solubility in common solvents (ethers, aromatic and saturated hydrocarbons) is very high. Cryoscopy in benzene shows that the compounds are monomeric in solution, like the related compounds Cp^*_2TiX;[6a] the molecular structure of **5** (vide infra) indicates that they are monomers in the solid state as well. The compounds are quite volatile, and several can be sublimed, although some thermal decomposition and cosublimation of thermolysis product Cp*FvTi cannot be avoided.[16,17] The best technique for obtaining analytically pure, crystalline compounds is low-temperature crystallization from Et_2O or pentane.

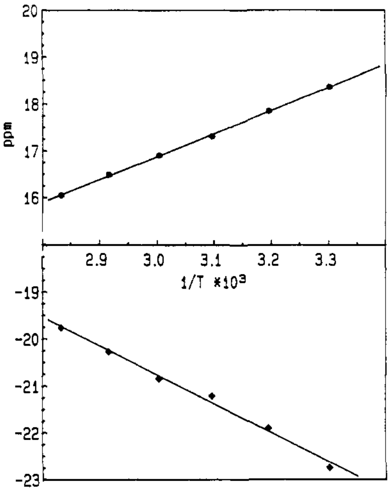

Figure 1. Curie behavior of ^{1}H NMR shifts of Cp^*_2TiMe (**2**).

NMR Spectra. Compounds **2–11** are paramagnetic d^1 titanium(III) systems. Until now NMR spectroscopy has found only limited use in the identificantion and structure assignment of paramagnetic molecules, although the study by Köhler et al. on paramagnetic organovanadium and chromium compounds Cp_2VR[22] and $CpCrR_2(PMe_3)$[22b] and work by Fischer on paramagnetic f-element compounds[23] demonstrate that NMR (^{1}H, ^{2}H, and ^{13}C) can be very helpful as an analytical tool. We have recorded ^{1}H NMR spectra of compounds **2–11** in toluene-d_8 or benzene-d_6 at room temperature and ^{2}H NMR spectra (toluene solution) of partially deuterated alkyl compounds **2**-d_3, **3**-d_5, **4**-d_3, **4**-d_7, **9**-d_3, and **11**-d_5 (Table III). The ^{1}H NMR spectra show, as expected,[24] broad and strongly shifted resonances with a shift inversely related to temperature, the normal Curie behavior of monomeric paramagnetic species in solution (Figure 1, Table IV). The Cp* resonances of all compounds are observed as single, broad (fwhm varying from 0.88 kHz (**10**) to 5.5 kHz (**7**)) lines, located between δ 14.5 and 20.9 ppm. Both position and width are close to those of the related complexes Cp^*_2TiX[6a] with X = anionic ligand. As noted for bidentate ligands X, the presence of bidentate R leads to very broad Cp* signals. No clear relation between the shift of the Cp* resonance and the nature of group R is evident. The Cp* resonances of simple alkyl derivatives **2–5** are spread over the full shift range so far observed for compounds Cp^*_2TiR and Cp^*_2TiX.

The ^{1}H NMR spectra of most compounds show resonances associated with group R protons that can be identified on the basis of the signal intensities. Full as-

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Table III. ^{1}H and ^{2}H NMR and EPR Data for Cp^*_2TiR

R	compd no.	^{1}H NMR[a]							^{2}H NMR[a]		EPR[b]	
					Cp*		R		R			
		solvent	temp, °C	field, MHz	δ	WHM[c]	δ	WHM[c]	δ	WHM[d]	g[e]	ΔH[f]
Cl	1	benzene-d_6	18	200	14.4	1.00					1.956	60.0
Me	2	toluene-d_8	22	300	19.0 (30 H)	1.23	−23.5 (3 H)	1.73	−22.2	34	1.957	67.5
Et	3	benzene-d_6	18	200	19.8	1.22	[g]		124.9 (2 D) −78.8 (3 D)	2300 945	1.972	18.9
n-Pr	4	toluene-d_8	−30	200	20.9 (30 H)	1.65	0.90 (3 H) [g]	0.36	24.6 (2 D) 16.1 (2 D) −5.4 (3 D)	170 161 9.6	1.953	15.5[h]
CH_2CMe_3	5	toluene-d_8	22	300	14.5 (30 H)	1.35	5.63 (9 H)[g]	0.40			1.951	20.8
CH_2Ph	6	toluene-d_8	21	300	15.7 (30 H)	1.40	10.36 (1 H)[g] 9.26 (2 H)	0.10 0.07			1.948	24.0
η^3-C_3H_5	7	toluene-d_8	22	300	18.9	5.52	[g]				1.992	4.7
η^3-C_3H_4Me	8	benzene-d_6	20	200	19.8	4.50	[g]				1.992	4.4
$CH{=}CH_2$	9	toluene-d_8	22	300	19.4 (30 H)	0.96	9.19 (1 H) [g]	0.10	28.3 (1 D) 7.94 (1 D) −53.0 (1 D)	54.7 4.4 250	1.952	86.0
$C{\equiv}CMe$	10	benzene-d_6	19	200	18.7	0.88	1.03 (3 H)	0.07	-		1.941	49.0
Ph	11	toluene-d_8	22	300	17.4 (30 H)	1.18	13.4 (1 H) 0.21 (2 H) [g]	0.21 0.19	23.3 (2 D, o) 13.3 (1 D, p) 0.3 (2 D, m)	57.0 9.6 8.7	1.954	51.5

[a] ^{1}H NMR: Solutions (0.2–0.4 M) in benzene-d_6 or toluene-d_8, shifts relative to residual protons in the solvent (benzene-d_6, δ 7.15; toluene-d_8, δ 6.98), downfield positive, spectral range studied ±300 ppm. ^{2}H NMR: solutions (0.2–0.4 M) in toluene at 22 °C, shifts relative to residual deuterons in solvent (δ 6.98), field 46.06 MHz. [b] In pentane (ca. 10^{-2}–10^{-3} M) at 20 °C. [c] Widths at half maximum (kHz). [d] Widths at half-maximum (Hz). [e] Relative to DPPH at g = 2.0037. [f] Peak to peak distance (G) measured peak to peak in the first-derivative spectrum. [g] Protons not (all) observed. [h] Spectrum at −20 °C.

Table IV. ^{1}H NMR Data for 2 in Toluene-d_8 at Various Temperatures

T, °C	Cp* δ, ppm	Me δ, ppm	T, °C	Cp* δ, ppm	Me δ, ppm
30.0	18.38	−22.74	60.0	16.91	−20.84
40.0	17.86	−21.90	70.0	16.49	−20.27
50.0	17.32	−21.21	80.0	16.05	−19.76

signment of all protons is only possible for **2** and **10**. For the other compounds only part of the protons can be identified. The methyl resonances of the propyl ligand in **4**, the neopentyl ligand in **5**, and the propynyl ligand in **10** are observed between 0.9 and 5.6 ppm as rather narrow lines (fwhm < 400 Hz). For the phenyl ligand in **11**, the meta and para protons are observed. Two resonances of the phenyl group of the benzyl ligand in **6** with a ratio of 1 (δ 10.36 ppm) to 2 (δ 4.26 ppm) are tentatively assigned to the para and meta hydrogen atoms. In compounds **7** and **8** the resonances for the allylic ligand R were not located. For **9** only one of the three protons of the vinyl ligand is observed. In general it seems that protons in α- and β-positions interact too strongly with the paramagnetic metal center to give observable ^{1}H NMR signals. It is very likely that extreme broadening of the signals is the reason that these resonances are missing and not a chemical shift to outside the frequency range studied (±300 ppm). This is indicated by ^{2}H NMR spectra of alkyl compounds in which the alkyl ligand has been deuterated, **2**-d_3, **3**-d_5, **4**-d_3, **4**-d_7, **9**-d_3, and **11**-d_5.

^{2}H NMR spectroscopy has been used successfully for the structure assignment of paramagnetic Cr(III) complexes[22a,25] due to a dramatic narrowing of the ^{2}H NMR resonances compared to ^{1}H NMR signals.[26] This narrowing is also observed for the compounds Cp^*_2TiR and leads to the observation of all deuterons of the deuterated alkyl groups R. The shifts are quite comparable to those measured for ^{1}H NMR observable alkyl protons in compounds **2**–**4**. The line narrowing factor is about 40 for the methyl ligand in **2** as well as for the methyl group of the propyl ligand in **4**. If an average ratio of 40 is taken for the other resonances as well, widths between 3.7 and 6.8 kHz are estimated for the ^{1}H NMR signals of the α- and β-protons of the propyl ligand of **4**. For the ethyl compound the effect is even more dramatic: widths of 92 and 38 kHz are estimated for the α- and β-protons, respectively. It is obvious that in ^{1}H NMR spectra these extremely broad resonances are not observed. With respect to the chemical shifts of the various α- and β-deuterons there is no apparent fixed, small range where they are located. The α-deuterons are spread from −22.2 ppm (**2**) to 124.9 ppm (**3**), and β-deuterons cover the range−78.8 ppm (**3**) to 16.1 ppm (**4**). Both the large spread in chemical shift and the extreme broadness of the ethyl α- and β-deuteron resonances indicate that this ligand has a special way of bonding to the metal, and IR evidence (vide infra) suggests that there are β-agostic interactions.

At the moment we have no explanation for the striking features of the ^{1}H and ^{2}H NMR spectra, such as the extreme widths of the Cp* ^{1}H NMR signals for **7** and **8**, the very broad ^{2}H NMR resonances of the ethyl group in **3** compared to the corresponding resonances in **2** and **4**, or the spread in chemical shifts between the various deuterated alkyl groups studied. It is, however, clear from our results that both ^{1}H and ^{2}H NMR spectra can be quite useful for characterization and also for monitoring reaction mixtures with Cp* or other well-resolved resonances as probes.

EPR Spectra. The room-temperature solution (pentane, 10^{-2}–10^{-3} M) EPR spectra (Table III) of compounds **2**–**11** all show singlets with no hyperfine splitting due to interactions with hydrogen nuclei of ligands R observed. Titanium isotope satellites are missing as well. A change of solvent (Et_2O, THF, toluene), dilution (down to ca. 10^{-5} M), nor a lowering of the temperature produces better resolution. The averaged g values of the resonances range from g = 1.992, for the allyls **7** and **8**, to g = 1.941–1.957 for the others. The ethyl **3** with g = 1.972 is intermediate,

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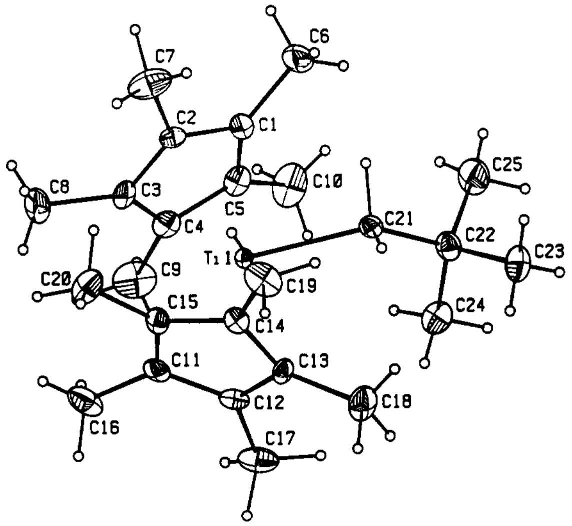

Figure 2. Perspective ORTEP drawing of $Cp^*_2TiCH_2CMe_3$ (**5**). All non-hydrogen atoms are represented by their thermal displacement vibrational ellipsoids drawn to encompass 50% of the electron density; the hydrogen atoms are drawn with an arbitrary radius.

Table V. Selected Bond Lengths (Å) and Angles (deg) for $Cp^*_2TiCH_2CMe_3$ (5)

	Bond Lengths		
Ti-C(21)	2.231 (5)		
Ti-CE(1)[a]	2.104 (2)	Ti-CE(2)[b]	2.094 (2)
Ti-C(1)	2.445 (4)	Ti-C(11)	2.434 (4)
Ti-C(2)	2.365 (4)	Ti-C(12)	2.392 (4)
Ti-C(3)	2.419 (3)	Ti-C(13)	2.412 (4)
Ti-C(4)	2.420 (5)	Ti-C(14)	2.397 (4)
Ti-C(5)	2.461 (4)	Ti-C(15)	2.431 (4)
Cp*(1) (C(1)-C(5))		Cp*(2) (C(11)-C(15))	
C-C ring[c]	1.412 (3)	C-C ring[c]	1.411 (3)
C-C exo[d]	1.490 (3)	C-C exo[d]	1.492 (3)
C(21)-C(22)	1.559 (6)	C(22)-C(24)	1.529 (6)
C(22)-C(23)	1.526 (7)	C(22)-C(25)	1.522 (7)
	Bond Angles		
CE(1)-Ti-CE(2)	139.4 (3)		
CE(1)-Ti-C(21)	108.4 (1)	CE(2)-Ti-C(21)	111.4 (1)
Cp*(1) (C(1)-C(5))		Cp*(2), (C(11)-C(15))	
C-C-C ring[c]	107.9 (2)	C-C-C ring[c]	108.0 (2)
C-C-C exo[d]	125.4 (2)	C-C-C exo[d]	125.6 (2)
Ti-C(21)-C(22)	131.1 (3)		
C(21)-C(22)-C(23)	111.0 (4)	C(23)-C(22)-C(24)	108.3 (4)
C(21)-C(22)-C(24)	111.7 (4)	C(23)-C(22)-C(25)	106.7 (4)
C(21)-C(22)-C(25)	111.4 (4)	C(24)-C(22)-C(25)	107.4 (4)

[a] CE(1) = C(1)-C(5) ring centroid. [b] CE(2) = C(11)-C(15) ring centroid. [c] Average distances and angles in the ring. [d] Average distances and angles between ring and methyl carbon atoms.

though closer to the alkyl and aryl compounds than to the allyls. The large variation in *g* values indicates that the unpaired electron resides in allyls **7** and **8** in an orbital different from where it is in the other compounds. This is confirmed by the remarkable difference in the width of the signals. The allyls **7** and **8** have narrow lines (fwhm 4.5 G), whereas the others are much broader (fwhm between 5.5 and 86.0 G). The narrow allyl signals are not flanked by titanium isotope satellites either, indicating that this coupling is much smaller than that normally observed for Cp^*_2TiX and related complexes, where isotope coupling constants between 8 and 14 G have been observed.[6a]

IR Spectra. The IR spectra show characteristic absorptions of the Cp* ligands (at 2720 (w), 1480 (m), 1430 (m), 1370 (s), 1020 (m), and 800 (w) cm^{-1}) and of the group R. Some spectra give information with respect to the bonding of R to the metal and are discussed briefly. The ethyl compound **3** shows weak absorptions at 2300–2400 cm^{-1} which are shifted to 1820 and 1770 cm^{-1} in the selectively deuterated compound **3**-d_5 and strongly indicate β-agostic C–H–Ti interactions.[27] Surprisingly, the propyl **4** does not show these absorptions, although the required C–H bonds are present. Steric hindrance by the methyl substituent probably makes the geometry in a β-agostic conformation less favorable. The benzyl **6** shows an intense phenyl ring stretching mode at 1595 cm^{-1}. Such an intense absorption seems to be characteristic for η^1-benzyl,[28] and we assume that this bonding mode is present in **6** as well. The low-energy position of the C=C stretch in the allyls **7** and **8** (1500 and 1530 cm^{-1}, respectively) indicates that these ligands are η^3-bonded,[25] thus forming 17-electron Ti(III) species like the cyclopentadienyl analogues Cp_2TiR.[29] The vinyl **9** shows a weak ν(C=C) signal at 1550 cm^{-1}, and the propynyl **10** has the acetylenic stretching mode at 2080 cm^{-1}. This is a good indication that these ligands are σ-bonded to titanium without further interaction of their unsaturated system. This is in contrast with the observed coupling of the alkynyl ligand that has been observed for the cyclopentadienyl compounds $Cp_2TiC{\equiv}CR$[30] and very recently for samarium systems as well.[31]

Structure of $Cp^*_2TiCH_2CMe_3$ (5). The structure shows that crystals of **5** are built of discrete monomeric units of $Cp^*_2TiCH_2CMe_3$ (Figure 2), with four discrete molecules per unit cell. Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are given in Table II, with relevant bond lengths and angles in Table V. The molecule shows the typical bent-sandwich geometry. The pentamethylcyclopentadienyl ligands are staggered; the metal to ring-centroid distances (Ti–CE(1) = 2.104 (2) Å, Ti–CE(2) = 2.094 (2) Å) and the angle (CE(1)–Ti–CE(2) = 139.4°) are normal and close to the values reported for related Cp^*_2Ti systems.[3b,6a]

The molecule is sterically congested, as is illustrated by the deviations of the cyclopentadienyl methyl substituents from the ring planes. The largest deviations are at the back of the bent sandwich (C(8), 0.43 Å; C(16), 0.28 Å; C(20), 0.23 Å), where the cyclopentadienyl ligands touch. Also at the front of the wedge, where the bulky neopentyl group is located, the Cp* methyl groups are pushed out of the ring planes (C(6), 0.30 Å; C(10), 0.23 Å; C(18), 0.37 Å). The other ring methyl substituents have much smaller deviations (0.09–0.16 Å). The rather large obtuse angle Ti-C(21)-C(22) (131.1 (3)°) indicates significant steric repulsion between the cyclopentadienyl rings and the *t*-Bu group of the neopentyl ligand. This seems normal for early-transition-metal (e.g. Zr,[32] Ta,[33] Y[34]) and f-element (Lu,[35] Th[36]) neopentyl and (trimethylsilyl)methyl com-

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pounds. There are short nonbonding contacts between Ti and C(22) (3.461 (5) Å), and C(24) (3.645 (5) Å), respectively 0.51 and 0.33 Å shorter than the sum of the van der Waals radii.

When Ti–C σ-bonds in cyclopentadienyl and dicyclopentadienyl systems are compared, it is clear that these seem to be rather independent of the formal oxidation state of the metal. The reported values range from 2.332 (2) Å in $\mathrm{Cp_4Ti}$[37] to 2.08 (1) Å in $\mathrm{Cp^*Ti(CH_2Ph)_3}$,[37b] with Ti–C = 1.988 (10) Å in the cationic complex $\mathrm{[Cp^*_2TiMe(THF)]^+}$.[3b] The Ti–C σ-bond in **5** is 2.231 (5) Å, only slightly longer than those reported for other d^1 compounds $\mathrm{Cp_2TiR}$[38] (R = aryl; Ti–C varies from 2.216 (7)[38c] to 2.096 (4)[38d] Å), but perfectly in the normal range.

The position of the neopentyl ligand with respect to the bisecting plane of the $\mathrm{Cp^*_2}$ wedge is quite interesting. The metal atom, C(21), C(22), and C(24) (torsion angle Ti(1)–C(21)–C(22)–C(24) = –21.1 (5)°) are approximately in this plane, presumably as the result of minimalization of steric repulsion rather than of agostic interactions between the electron-deficient metal and C–H or C–C bonds of the neopentyl ligand. There is no α-agostic interaction. The distances of Ti to H(211) and H(212) (2.65 (3) and 2.63 (3) Å, respectively) are much longer than those observed for the agostic CH bond in the α-CH–Ti interaction in $\mathrm{Ti(Me)Cl_3(dmpe)}$[27] (Ti–H = 2.03 (3) Å). They are comparable with the other C–H bond distances (2.56 (4) Å and 2.68 (3) Å, respectively). The geometry and Ti–H distances for the C(24) methyl group exclude γ-agostic interactions as well. A final comment is made with respect to the location of the neopentyl ligand. Theoretical considerations on d^1 $\mathrm{Cp_2MR}$ systems predict that the M–R bond will deviate from the plane formed by CE(1)–Ti–CE(2). An estimate of about 30° was made for R = H[39] and R = Me.[40] The compound under discussion here is also expected to show a similar feature, and indeed a deviation of 10.8° is observed. Whether this is indeed caused by electronic effects is not clear, since steric hindrance would also result in the same type of distortion.

Thermal Decomposition Studies. The compounds $\mathrm{Cp^*_2TiR}$ (**2–11**) are thermally much more stable than the cyclopentadienyl analogues $\mathrm{Cp_2TiR}$.[5] While $\mathrm{Cp_2TiMe}$ decomposes readily at –80 °C, **2** is stable up to about 80 °C. Similar stabilization is observed for the phenyl compound. $\mathrm{Cp_2TiPh}$ decomposes at room temperature, but **11** can be heated to 150 °C before thermolysis sets in at an appreciable rate. Other compounds show similar effects. Unlike compounds $\mathrm{Cp_2TiR}$, the thermolysis of $\mathrm{Cp^*_2TiR}$ can be studied in detail and identification of all products is possible. It appears that both in solution and in the solid state the thermolysis proceeds according to eq 3. The fulvene compound **12** is obtained as the exclusive

$$\mathrm{Cp^*_2TiR} \xrightarrow{\Delta} \underset{\mathbf{12}}{\mathrm{Cp^*FvTi}} + \mathrm{RH} \qquad (3)$$

organotitanium compound for the thermally least stable alkyls **2–6**. The thermally more robust complexes **7–11** need temperatures where **12** itself starts to decompose with hydrogen loss from the fulvene ligand and formation of the allyl diene compound $\mathrm{Cp^*(\eta^7\text{-}C_5Me_3(CH_2)_2)Ti}$.[17] The hydrocarbon RH is the only organic product formed. Other compounds such as coupling products R–R or olefins R(–H) indicating radical formation or β-hydrogen abstraction are not found, not even for β-hydrogen-containing ligands R. These two remarkable features of the thermolysis, i.e. the clean stoichiometric decomposition and the unexpected hydrogen abstraction from a Cp* ligand, prompted us to study the thermolysis of compounds **2–4** in detail. Preliminary kinetic measurements and deuterium labeling studies indicate that the process of thermal decomposition is not a simple intramolecular H-abstraction from a pentamethylcyclopentadienyl ligand by a leaving group R. The study is in progress, and the results will be published separately.[41]

Reactivity Studies. The Ti–C bond in compounds $\mathrm{Cp^*_2TiR}$ (**2–11**) has all the characteristics of a "highly polar" M–C bond. The compounds are extremely air-sensitive and react with active proton reagents (water, alcohols, carboxylic acids, hydrogen halides, etc.) with quantitative liberation of RH (eq 4). Various alkoxides,

$$\mathrm{Cp^*_2TiR} + \mathrm{HX} \rightarrow \mathrm{Cp^*_2TiX} + \mathrm{RH} \qquad (4)$$

$$\mathrm{X} = \mathrm{OR'},\ \mathrm{O_2CR'},\ \text{halide}$$

carboxylates, and halides have been prepared in this way and identified spectroscopically (IR, NMR) by comparison with authentic samples.[6a] Terminal acetylenes $\mathrm{RC{\equiv}CH}$ give a similar reaction. When **2** was treated at –80 °C with 1 mol of $\mathrm{CH_3C{\equiv}CH}$, methane and $\mathrm{Cp^*_2TiC{\equiv}CCH_3}$ (**10**) were rapidly formed in quantitative yield. Excess propyne is catalytically dimerized exclusively to the *gem*-enyne $\mathrm{CH_2{=}C(Me)C{\equiv}CMe}$. Highly selective catalytic dimerization of terminal acetylenes is a common feature of $\mathrm{Cp^*_2MR}$ (R = H, alkyl) systems of group 3 and 4 metals and lanthanides. It has been reported for systems based on $\mathrm{Cp^*_2TiCl_2}/i\text{-}\mathrm{PrMgBr}$,[42] $\mathrm{Cp^*_2ScR}$ (R = H, Me),[2g] and $\mathrm{Cp^*_2YR}$.[2h] We have studied the system $\mathrm{Cp^*_2TiH/RC{\equiv}CH}$ in detail, and the results will be reported in a forthcoming paper.[19]

Coordination Chemistry. Compounds $\mathrm{Cp^*_2TiR}$ are coordinatively unsaturated 15-electron systems but show little tendency to relieve this unsaturation, e.g. by dimerization or adduct formation with Lewis bases such as THF, amines, or phosphines. Also, complexation of salts (e.g. LiX or $\mathrm{MgX_2}$) or formation of anionic species $\mathrm{[Cp^*_2TiR_2]^-}$, which are common for lanthanide and the heavier group 3 elements Y and La,[21] was not observed. In fact, $\mathrm{Cp^*_2TiR}$ compounds behave in this respect much like their scandium analogues $\mathrm{Cp^*_2ScR}$.[2g]

In contrast with the case for titanium, the very stable 16-electron scandium adduct $\mathrm{Cp^*_2ScMe{\cdot}THF}$ was reported.[2g] The scandium ionic radius is only about 0.07 Å larger than for titanium, as follows from the pentamethylcyclopentadienyl centroid to metal distances in similar complexes (2.17 Å for $\mathrm{Cp^*_2ScCH_3}$ vs 2.10 Å for **5**). The absence of a stable THF adduct of **2** therefore does not seem to be steric in origin, but rather the result of the diminished Lewis acidity. In addition an acetone adduct of **2** was isolated. Ligands with small cone angles such as CO, nitriles, and isonitriles do easily form the adducts $\mathrm{Cp^*_2TiR{\cdot}L}$. However, these are generally not stable and react further to give insertion, disproportionation, or

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coupling products (vide infra). In contrast with cyclopentadienyl analogues Cp_2TiR, compounds Cp^*_2TiR do not react with dinitrogen to form complexes $(Cp^*_2TiR)_2N_2$. When a solution of **2** or **11** in toluene was cooled under N_2 (1 bar) to −100 °C, the very characteristic deep blue color of the dinitrogen complexes was not observed. This is very surprising, since titanium dinitrogen complexes $(Cp_2TiR)_2(\mu\text{-}N_2)$[43] and $(Cp^*_2Ti)_2(\mu\text{-}N_2)$[44] are formed very easily.

Ligand Exchange Reactions. Reaction of Cp^*_2TiR with an alkylating reagent such as an aluminum alkyl leads to exchange of alkyl ligands. For example, mixing **3** with a stoichiometric amount of $AlMe_3$ gave quantitatively $AlMe_2Et$ and **2** (eq 5). Reaction of **3** and $AlMeCl_2$ led to rapid exchange of chlorine and the alkyl on titanium (eq 6). This is a convenient way of transforming compounds Cp^*_2TiR back to Cp^*_2TiCl. Transfer of a carbyl ligand from titanium to aluminum has been claimed earlier.[45] It appears that organotitanium compounds are (trans)alkylating reagents for aluminum alkyls and halides, an observation not without relevance for chain transfer reactions in olefin polymerization with classical Ziegler–Natta systems.[46] Exchange of R was also observed between Cp^*_2TiR and Grignard reagents R^1MgCl, although for **3** this reaction is complicated by interference of an unexpected reduction of the magnesium compound.

$$\underset{\mathbf{3}}{\mathrm{Cp^*_2TiEt}} + \mathrm{AlMe_3} \rightarrow \underset{\mathbf{2}}{\mathrm{Cp^*_2TiMe}} + \mathrm{AlMe_2Et} \qquad (5)$$

$$\underset{\mathbf{3}}{\mathrm{Cp^*_2TiEt}} + \mathrm{AlMeCl_2} \rightarrow \underset{\mathbf{1}}{\mathrm{Cp^*_2TiCl}} + \mathrm{AlMeEtCl} \qquad (6)$$

When **3** was treated with MeMgCl at low temperatures (−80 °C), the expected exchange of ligand R and formation of **2** was only the minor reaction pathway. In addition, methane was evolved and the titanium ethene complex $Cp^*_2Ti(\eta^2\text{-}C_2H_4)$[47] was formed in 70% yield, together with metallic magnesium (eq 7). This reduction of a Grignard reagent by tervalent titanium[48] is analogous to the reduction of aluminum hydrides and alkyls by samarium(II).[49] At higher temperatures exchange becomes the dominant process and **2** and EtMgCl are the main products. In light of this reduction reaction, it is remarkable that metathesis between **1** and Grignard reagents is a very useful method for synthesis of compounds Cp^*_2TiR. Apparently two factors are important: first, the fact that at higher temperatures reduction seems less favorable than formation of a Ti–R bond and, second, formation of a stable titanium(IV) compound, e.g. $Cp^*_2Ti(\eta^2\text{-}C_2H_4)$, which supplies the driving force. The mechanism of the reduction reaction remains to be clarified. Possibly the intermediate anionic titanium species $[Cp^*_2Ti(Et)Me]^-[MgCl]^+$ is formed, from which methane is eliminated by β-H transfer.[50]

$$\underset{\mathbf{3}}{\mathrm{Cp^*_2TiEt}} + \mathrm{MeMgCl} \rightarrow \mathrm{Cp^*_2Ti(\eta^2\text{-}C_2H_4)} + \mathrm{CH_4} + 0.5\mathrm{Mg} + 0.5\mathrm{MgCl_2} \qquad (7)$$

Reaction with Carbon Monoxide. Carbonylation of metal carbyls of the early transition metals, lanthanides, and actinides of the type $Cp^*_2MR_n$ (n = 1, 2) is an intriguing subject. Initial acyl formation is followed by e.g. further CO insertion to give enedione diolate species[2c,51,52] or by reductive coupling of the acyls.[53] Tervalent titanium compounds Cp_2TiR react readily with CO, but the reactions are very complicated.[54] Formation of acyls, Cp_2TiCOR, has been established, but these react further, depending on the nature of R and the conditions applied, to give $Cp_2Ti(CO)_2$ and numerous other unidentified products. One of the effects of replacing cyclopentadienyl by permethylcyclopentadienyl ligands is that reactions are cleaner. Therefore, a study of carbonylation of Cp^*_2TiR was undertaken. At low temperatures ($T \approx -80$ °C) reaction took place quickly in pentane or toluene with formation of acyls (eq 8). The acyls are intensely colored dark blue complexes, thermally stable up to about 0 °C. For R = Me, Et they have been isolated and characterized by NMR and IR spectroscopy. The ν(CO) values (1530 cm^{-1} for R = Me, 1520 cm^{-1} for R = Et) indicate η^2-acyls. de Boer et al. have reported acyls Cp^*_2TiCOR (R = Me, CH_2CMe_3) through carbonylation of Cp^*_2TiR, but no details on synthesis and physical characteristics were given.[7] Above 0 °C the acyls are thermally unstable, both in solution and in the solid state, and give in the presence or absence of extra CO complex mixtures (NMR) of para- and diamagnetic compounds. $Cp^*_2Ti(CO)_2$ (NMR (benzene-d_6) δ = 1.64 ppm; IR ν(CO) 1948, 1865 cm^{-1}) is the only organotitanium compound that has been identified so far. Töpler pump experiments (room temperature, pentane or benzene solutions) indicate a variable uptake of 1.1–1.9 mol of CO per mol of Ti. Studies of the reaction of Cp^*_2TiR (**2**, **7**, **11**) with excess CO in benzene-d_6 at room temperature by ^1H NMR spectroscopy) showed that the reaction is fast but not clean. For **2** and **11** mixtures of paramagnetic and diamagnetic compounds were formed and, again, $Cp^*_2Ti(CO)_2$ could be identified (accounting for about 10–20% of the original Cp^*_2TiR). Interestingly, for **2** a resonance at δ −0.61 ppm indicates the formation of $Cp^*_2TiMe_2$ (comparison with an authentic sample (benzene-d_6) δ 1.73 (Cp*, 30 H), −0.61 (Me, 3 H) ppm), thus suggesting a CO-induced disproportionation to $Cp^*_2Ti(CO)_2$ and $Cp^*_2TiMe_2$, as has been found for the system Cp^*_2TiCl/CO.[6d] Similar observations were made for the phenyl compound **11**. The allyl compound **7** reacted under the same conditions quickly (within 1 h) to give a mixture of exclusively diamagnetic compounds. $Cp^*_2Ti(CO)_2$ now accounts for a substantial amount (ca. 30%) of the original compound **7**. Reaction of the product mixture with HCl gas resulted in formation of some $Cp^*_2TiCl_2$ (^1H NMR δ = 1.85 ppm), together with several unidentified products. GC–MS analysis of the organic fraction of the HCl reaction

$$\mathrm{Cp^*_2TiR} + \mathrm{CO} \rightarrow \mathrm{Cp^*_2TiCOR} \qquad (8)$$

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mixture showed many components present, all apparently of Cp* origin. No component could be identified as stemming from carbonylation of allyl ligands alone, e.g. RCHOH, R_2CO, or R_3COH. These would have been present if the reaction of **7** with CO were analogous to that of $Cp_2TiC_3H_5$.[55] Instead, the products that could be identified indicate insertion of the allyl–acyl fragment to the Cp* ligand.[56] This is analogous to the observation by de Boer,[7] who reports migration of the acyl in Cp*$_2$TiCOMe, assisted by $[CpMo(CO)_3]_2$. Recently, a similar insertion of an acyl into the Cp* ligand has been observed for tantalum.[57] Interestingly, in our system ring expansion by insertion of the acyl carbon atom in the five-membered ring, followed by cleavage of the acyl C=O bond, oxygen transfer to titanium, and formation of a pentamethylbenzene derivative, viz. 1-allylpentamethylbenzene,[53] seems to be possible without the assistance of external Lewis base.

In conclusion it is noted that reaction of Cp*$_2$TiR with CO is still a complicated process where acyl formation, disproportionation to Ti(II) and Ti(IV) compounds, and nucleophilic attack of the cyclopentadienyl groups combined with ring expansion can all take place.

Reaction with Isonitriles. Isonitriles, RN≡C, generally are considered to be useful model substrates for CO reactions. They are often used when CO itself gives intractable mixtures, e.g. due to subsequent reactions of initially formed acyls.[58] In the case of Cp*$_2$TiMe (**2**) the bulky isonitrile $Me_3CN{\equiv}C$ gives a quick and clean insertion to produce the η^2-iminoacyl **16**, with ν(C=N) at 1590 cm^{-1}. Oxidation of **16** with $PbCl_2$ gives the dimagnetic iminoacyl chloride Cp*$_2$Ti(CMe=NCMe$_3$)Cl, which probably has an η^2-iminoacyl ligand (ν(C=N) 1575 cm^{-1}, ^{13}C NMR iminoacyl C resonance at $\delta = 231$ ppm[59]). The fact that η^2-coordination is still favored in an apparently sterically crowded Cp*$_2$Ti(R)Cl complex is a good indication how strongly Lewis acidic this Ti(IV) center is. Insertion of an isonitrile into the polar Ti–C bond is expected and has been observed before for Cp_2TiR compounds;[5] it also is the normal reaction in ionic complexes[3e] $[Cp_2TiR(L)]^+$ and in the neutral group 3 and lanthanide compounds Cp*$_2$Mr.[60]

Reaction with Carbon Dioxide. Metal carboxylate formation is the most frequently observed reaction of metal–carbon bonds with CO_2.[61] It is also the dominant one for the complexes Cp*$_2$TiR. They react in solution smoothly with gaseous CO_2 at room temperature, with the exception of **11**, which appears to react very slowly if at all. The alkyls with β-H present an unprecedented hydrogen transfer from the alkyl ligand to the incoming CO_2 molecules with formation of the formate Cp*$_2$TiO$_2$CH[6b] and quantitative extrusion of olefin R–H (eq 9). This β-H

$$\mathrm{Cp^*_2TiCH_2CH_2R + CO_2 \rightarrow Cp^*_2TiO_2CH + RCH{=}CH_2} \qquad (9)$$

transfer and olefin extrusion vs insertion of various unsaturated substrates is a dominant feature of the reactivity of compounds Cp*$_2$TiR with β-H in group R. At the moment this process is under further investigation and details will be published separately.[59]

Reaction with Olefins. The role of coordinatively unsaturated titanium alkyls in olefin polymerization is the subject of continuous interest and discussion. So far no well-defined neutral titanium-based molecular system with established activity for catalytic olefin polymerization has been described. Recently cationic species $[Cp^\dagger_2TiMe(L)]^+$ ($Cp^\dagger = \eta^5$-C_5Me_5, η^5-C_5H_5; L = Lewis base) have been reported[3,4] which polymerize ethene only if both the cyclopentadienyl ligand and the Lewis base meet certain requirements. Catalytic activity has been observed for the normal cyclopentadienyl complex $[Cp_2TiMe(L)]^+$ when L is an ether ligand (THF, Et_2O, or $PhOCH_3$).[3c] Although the complexes Cp*$_2$TiR discussed here formally meet the requirements for catalytic activity, viz. a M–C bond and a vacant coordination site, they do not polymerize or oligomerize ethene or propene. Various compounds (**2**–**4**, **9**–**11**) were tested (room temperature, toluene, 1 atm of ethene, 48 h), but no ethene insertion into the Ti–C bond was observed. Also, under more drastic conditions (50 °C, 10 atm of ethene, 100 h) compound **2** was recovered unchanged. This is in sharp contrast to the isostructural compounds Cp*$_2$ScR, which are living catalysts for the oligomerization of ethene.[2g,f,62] The diminished Lewis acidity of the metal center has obvious consequences for polymerization activity. Apparently, the tervalent Cp*$_2$TiR system cannot induce sufficient positive charge at the β-carbon atom of an incoming ethene molecule to reach the polar transition state for migratory insertion.

A quite unexpected reaction was observed when solutions of alkyls **3** and **4**, which possess β-H, were exposed to ethene or propene. In these systems neither oligomerization nor polymerization was observed but fast exchange of olefins took place. As an example we give here the reaction of the ethyl compound **3** with excess propene (eq 10). The reaction is reversible, and when the conditions are changed and an excess of ethene is supplied, **4** easily produces **3**. This exchange of olefin is typical for titanium alkyls Cp*$_2$TiCH$_2$CH$_2$R and has been observed with a variety of unsaturated substrates such as nitriles, alkynes, ketones, and carbon dioxide.

$$\underset{\mathbf{3}}{\mathrm{Cp^*_2TiEt}} + \mathrm{MeCH{=}CH} \rightleftarrows \underset{\mathbf{4}}{\mathrm{Cp^*_2Ti(}n\mathrm{\text{-}Pr)}} + \mathrm{CH_2{=}CH_2} \qquad (10)$$

Reaction with But-2-yne. With an excess of but-2-yne compound **2** reacted slowly at room temperature to give cis insertion of the alkyne into the Ti–C bond and formation of a substituted vinyl compound, Cp*$_2$TiC(Me)=CMe$_2$ (**9a**). With a stoichiometric amount of HCl the latter compound gave Cp*$_2$TiCl (**1**) and 1 mol of 2-methyl-2-butene (NMR). The partly deuterated compound **2**-d_3 was treated with HCl after reaction with but-2-yne. The methyl-d_3-2-butene obtained was identified (^{1}H NMR) as the cis isomer, thus demonstrating that insertion of but-2-yne in the Ti–C bond gives indeed a cis-vinylic derivative as normally observed in organo-transition-metal chemistry.[59]

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The ethyl compound **3** reacted completely differently with but-2-yne. Instead of insertion into the Ti–Et bond, extrusion of ethene and formation of the new vinyl $Cp^*_2TiC(Me){=}C(H)Me$ (**9b**) was observed. Treatment with HCl again gave **1** and *cis*-2-butene. This apparent transfer of β-H from the ethyl ligand to the substrate, i.e. but-2-yne, fits the general pattern of reactivity of titanium alkyls Cp^*_2TiR with β-H on the alkyl ligand.

Concluding Remarks. Cp^*_2TiCl is an excellent starting material for a wide range of monomeric compounds Cp^*_2TiR by reaction with alkali-metal or Grignard compounds. These paramagnetic compounds have characteristic NMR (^1H and ^2H) and EPR spectra, which can be used for identification and for monitoring their reactivity. The Ti–C bond in Cp^*_2TiR is polarized with negative charge concentrated on the ligating carbon atom. The compounds show the expected reactivity toward polar substrates when R is aryl, vinyl, benzyl, or an alkyl ligand lacking β-hydrogen. Substrates X–H with active hydrogen split off R quantitatively as RH. Unsaturated substrates, e.g. CO, CO_2, and isonitriles, insert into the Ti–C bond. When R is an alkyl ligand with β-hydrogen, the reactivity with unsaturated substrates, e.g. CO_2, alkenes, or alkynes, is dominated by extrusion of olefin R(–H).

Nonpolar substrates such as internal alkynes insert slowly into the Ti–C bond. Olefins do not insert into the Ti–C bond at all. The necessary transition state for migratory insertion is not reached in these processes. This illustrates the decreased Lewis acidity of tervalent permethyltitanocene alkyls compared with that of group 3 and lanthanide congeners and also with the cationic polymerization catalysts $[Cp^*_2MR]^+$.

Intermolecular reactions are not observed, reflecting the effectiveness of bulky Cp* ligands in the formation of reactive single-site metal centers. Paramagnetic organometallic compounds of the early transition metals have a rich and exciting chemistry, and this study demonstrates that they have so far unjustly been neglected in organometallic research.

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Supplementary Material Available: Tables of final fractional atomic and equivalent isotropic thermal parameters, anisotropic thermal parameters, and full bond lengths and angles for $Cp^*_2TiCH_2CMe_3$ (**5**) and details on experimental procedures and spectroscopic data for partially deuterated compounds Cp^*_2TiR and carboxylates $Cp^*_2Ti(\eta^2\text{-}O_2CR)$ (14 pages); a listing of observed and calculated structure factors for **5** (22 pages). Ordering information is given on any current masthead page.

(η^6-Naphthalene)(η^4-1,5-cyclooctadiene)ruthenium(0): Efficient Synthesis, Chemistry, and Catalytic Properties

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The ruthenium(0) complex (η^4-1,5-cyclooctadiene)(η^6-naphthalene)ruthenium(0), $Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})$ (**2**), is conveniently synthesized in 55–64% yield on a gram scale by treatment of $Ru(acac)_2(\eta^4\text{-}C_8H_{12})$ (acac = acetylacetonate) with sodium naphthalide. A preliminary ^1H NMR study of the rate of replacement of naphthalene by arenes in the presence of acetonitrile at room temperature has been made. The reaction is first order in **2** and approximately first order in acetonitrile up to $[CH_3CN]/[\mathbf{2}]$ ca. 3, but a higher order for the latter cannot be excluded. Benzene, toluene, and xylene (8 mol per mol of **2**) in THF-d_8 replace naphthalene at almost the same rate, but the reaction is slower when there are more than two methyl groups in the entering arene, the order being *p*-xylene > 1,2,4-trimethylbenzene > 1,2,3,4-tetramethylbenzene ≫ mesitylene. The results are consistent with the initial formation of labile intermediate η^4- or η^2-naphthalene complexes that are stabilized by acetonitrile, e.g., $Ru(\eta^4\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})(NCMe)$. Solutions of **2** in acetonitrile lose naphthalene to form a dinuclear μ-naphthalene complex $Ru_2(\eta^4\text{-}C_8H_{12})_2(\mu\text{-}C_{10}H_8)$ (**5**). The new η^6-arene complexes $Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})$ (arene = C_6H_5CN (**4**), 1,2,4-$C_6H_3Me_3$ (**6**), 1,2,3,4-$C_6H_2Me_4$ (**7**), $C_6H_5CH{=}CH_2$ (**9**), 1-Me-4-$CH_2{=}CMeC_6H_4$ (**10**), (*E*)-$C_6H_5CH{=}CHC_6H_5$ (**11**), $(C_6H_5)_3As$ (**14**), and $(2\text{-}MeC_6H_4)_3P$ (**15**) have been obtained from **2**, and the new ruthenium(II) complexes $[RuCl_2(\eta^6\text{-arene})]_2$ (**12**) and $Ru(O_2CMe)_2(\eta^6\text{-arene})$ (**13**) (arene = 1-Me-4-$CH_2{=}CMeC_6H_4$) have been prepared from **10**. Protonation of **2** with HPF_6 gives the hydridoruthenium(II) complex $[RuH(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})]PF_6$ (**16**), from which naphthalene is readily displaced by *p*-xylene or mesitylene to give $[RuH(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})]PF_6$. In the presence of acetonitrile and hydrogen (1–20 atm), **2** catalyzes the hydrogenation of olefins. It is much more active than $Ru(\eta^6\text{-arene})(\eta^4\text{-}C_8H_{12})$ (arene = C_6H_6, 1-Me-4-$Me_2CHC_6H_4$) under the same conditions, probably as a consequence of the ease of $\eta^6 \rightarrow \eta^4$ conversion for naphthalene.

Introduction

It is now well-established that η^5-indenyl complexes undergo substitution reactions more readily than corresponding η^5-cyclopentadienyl complexes, probably as a consequence of the stabilization of a η^3-indenyl transition state or intermediate.[1] A similar effect probably operates

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