conversion reaction, presumably by affecting the charge density at the reaction site. Estimates of the free energies of activation for the 1 → 2 isomerization are included in Table V, and the values for the alkyl systems are considerably higher than those of the aryl complexes. This reinforces the idea that electronic factors are important in determining the activation energy and hence the rate of the isomerization reactions.

Oxygenation of Complexes 2. When solutions of the complexes **2** are left exposed to the air, there is a slow conversion of **2** to the bridging acrylamide complexes **3**. A better way to achieve this conversion is through the deliberate oxygenation of **2** with Me_3NO in refluxing acetone.[1] When R is an aryl substituent, conversions of 50–90% are achieved within a few hours; smaller amounts of **3** are obtained with the alkyl systems. Since CO_2 is evolved in these reactions, there is oxygen transfer from Me_3NO to both CO and the imine carbon in **2**. It is known[18] that terminal carbonyls are most susceptible to attack by Me_3NO, and therefore **2a** is probably the reactive species in solution.

Summary and Conclusions

This study of the $\{(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3) + CNR\}$ system demonstrates that a single alkyne and isocyanide ligands can condense on a binuclear metal center to form a coordinated allenimine. The new ligands can adopt a number of coordination modes, and three are represented in the isomers revealed by NMR analysis of solutions of the product. The rates of formation of the allenimine complex and of interconversions between the isomeric forms are markedly dependent on the isocyanide substituent R. Rates are faster when R is an aryl group and slower for the alkyl systems. Electronic factors account for the rate differences, but steric factors can completely inhibit the reactions when R is very bulky.

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Registry No. **1** (R = Et), 110294-86-5; **1** (R = *i*-Pr), 98464-05-2; **1** (R = Cy), 98464-04-1; **1** (R = Ph), 110488-33-0; **1** (R = *p*-$MeOC_6H_4$), 110488-37-4; **1** (R = *p*-$NO_2C_6H_4$), 110488-41-0; **2a** (R = Et), 110488-21-6; **2a** (R = *i*-Pr), 110488-24-9; **2a** (R = Cy, 110488-27-2; **2a** (R = Ph), 110488-30-7; **2a** (R = *p*-$MeOC_6H_4$), 110488-34-1; **2a** (R = *p*-$NO_2C_6H_4$), 110488-38-5; **2b** (R = Et), 110488-22-7; **2b** (R = *i*-Pr), 110488-25-0; **2b** (R = Cy), 110488-28-3; **2b** (R = Ph), 110488-31-8; **2b** (R = *p*-$MeOC_6H_4$), 110488-35-2; **2b** (R = *p*-$NO_2C_6H_4$), 110488-39-6; **2c** (R = Et), 110488-23-8; **2i** (R = *i*-Pr), 110488-26-1; **2c** (R = Cy), 110488-29-4; **2c** (R = Ph), 110488-32-9; **2c** (R = *p*-$MeOC_6H_4$), 110488-36-3; **2c** (R = *p*-$NO_2C_6H_4$), 110488-40-9; $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$, 98395-25-6; CNPh, 931-54-4; $CNC_6H_4OMe\text{-}p$, 10349-38-9; $CNC_6H_4NO_2\text{-}p$, 1984-23-2.

Supplementary Material Available: Tables of thermal parameters, ligand geometries, and equations for planes for $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{\mu\text{-}C(NEt)C(CF_3)C(CF_3)\}$ and tables and figures of spectroscopic and kinetic data for $\{(\eta\text{-}C_5H_5)_2Rh_2(CO)\{\mu\text{-}C(NR)C(CF_3)C(CF_3)\}$ complexes (22 pages); a listing of structure factor amplitudes for $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{\mu\text{-}C(NEt)C(CF_3)C(CF_3)\}$ (16 pages). Ordering information is given on any current masthead page.

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[18] Luh, T.-Y. *Coord. Chem. Rev.* 1984, *60*, 255.

Synthesis and Molecular Structure of Chlorobis(tetraphenylcyclopentadienyl)titanium(III). Synthesis and Variable-Temperature ^1H NMR Study of Dichlorobis(tetraphenylcyclopentadienyl)titanium(IV)

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The reaction between either $TiCl_2$ or $TiCl_3$ and $K(C_5HPh_4)$ yields $(C_5HPh_4)_2TiCl$ (I). A green crystal of $(C_5HPh_4)_2TiCl\cdot CH_2Cl_2\cdot(C_4HO)_{1/2}$ obtained on recrystallization belongs to the triclinic space group $P\bar{1}$ with $a = 12.878$ (4) Å, $b = 14.586$ (5) Å, $c = 15.888$ (4) Å, $\alpha = 63.08$ (2)°, $\beta = 79.10$ (2)°, $\gamma = 63.67$ (2)°, $Z = 2$, and $V = 2385$ Å^3. The molecular structure, determined by refinement on 4281 reflections greater than or equal to $4\sigma(F_o)$, converged to $R_F = 6.13\%$ and $R_{wF} = 6.05\%$. The complex crystallizes as well-separated monomeric units with the tetraphenylcyclopentadienyl rings staggered to form an inter-ring centroid angle of 136.4° and a short Ti–Cl bond length of 2.312 (2) Å. The Ti–C bond lengths vary by 0.155 Å, and the phenyl groups bend away from Ti because of steric congestion at the metal. Solution EPR studies show evidence for free $(C_5HPh_4)_2TiCl$ ($g = 1.957$) and for a THF adduct ($g = 1.979$). Oxidation of I with AgCl cleanly produces $(C_5HPh_4)_2TiCl_2$ (II), which can be isolated. Dynamic ^1H NMR studies of II show evidence for restricted rotation of the phenyl substituents with $\Delta G^{\ddagger} = 9.6\text{–}10.0$ kcal/mol. Reduction of a THF solution of I with sodium naphthalide under argon produces an unstable brown mixture; however, addition of CO yields a species with IR absorptions at 1966 and 1892 cm^{-1}, which suggests the formation of $(C_5HPh_4)_2Ti(CO)_2$.

Introduction

Previous work on octaphenylmetallocenes has shown that the sterically bulky tetraphenylcyclopentadienyl ligand greatly reduces the reactivity of these complexes, as compared to the unsubstituted metallocenes.[2] Solid-state and solution structural studies have permitted an under-

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[2] Castellani, M. P.; Geib, S. J.; Rheingold, A. L.; Trogler, W. C. *Organometallics* 1987, *6*, 1703.

standing of how the phenyl groups interact within each cyclopentadienyl ring and between cyclopentadienyl rings.[2,3] Questions remain about the stabilities, reactivities, and conformations of bent bis(tetraphenylcyclopentadienyl)metal complexes. In our studies of reactions of $(C_5HPh_4)_2M$ compounds (M = V, Cr, Co, and Ni) no bent metallocene product was observed.[2] Thus, there was a question whether a first-row transition metal could accommodate a bent structure with two tetraphenylcyclopentadienyl ligands. Herein we report the synthesis, EPR spectra, reactivity, and solid-state structure of $(C_5HPh_4)_2TiCl$ (I) as well as its reduction chemistry. The synthesis and solution structure (by ^1H NMR spectroscopy) of $(C_5HPh_4)_2TiCl_2$ (II) are also discussed.

Experimental Section

All reactions of air- and moisture-sensitive materials were performed under a nitrogen or argon atmosphere employing standard Schlenk techniques. Solids were manipulated under argon in a Vacuum Atmospheres glovebox equipped with a HE-493 dri-train. Benzene, pentane, and tetrahydrofuran (THF) were refluxed over potassium–benzophenone ketyl and distilled under nitrogen. Dichloromethane was refluxed over CaH_2 and distilled under nitrogen. All solvents, used in to attempts to reduce compound I, were freeze–pump–thaw degassed a minimum of three times and placed under an argon atmosphere. Silver chloride was obtained from the reaction between $AgNO_3$ and NaCl in water (in the dark) followed by filtering and drying in vacuo. Potassium tetraphenylcyclopentadienide was prepared as described.[2] Sodium naphthalide (NaNp) solutions were prepared in THF solvent. The precise concentration of each solution (near 0.15 M) was determined by titration of the NaNp with diphenylacetic acid in THF with the green color of NaNp used to determine the endpoint. Titanium dichloride was prepared by a literature procedure.[4]

Cyclic voltammograms were recorded with a BAS-100 Electrochemical Analyzer and a Houston Instruments DMP-40 digital plotter. A conventional three-electrode cell [Pt button working electrode, Pt wire auxiliary electrode, and a Ag/Ag^+ (0.1 M $AgNO_3$ in CH_3CN) reference electrode] contained 2 mM solutions of the complex in electrolyte (0.25 M) solution. The supporting electrolyte (tetra-*n*-butylammonium perchlorate, Baker Polarographic Grade) was recrystallized twice from a mixture of ethyl acetate and isooctane. EPR spectra were recorded on a Varian E-3 spectrometer with use of diphenylpicrylhydrazyl as the field marker. Samples were cooled to 77 K by immersion in a liquid N_2 filled Dewar, and all solutions were 2×10^{-3} M in complex. The EPR samples were prepared by using Schlenk techniques or in the glovebox. Proton (300.152 MHz), ^2H (46.0745 MHz), and ^1H COSY NMR spectra were recorded on a GE QE-300 NMR spectrometer. Magnetic susceptibility measurements were made on a Varian EM-390 ^1H NMR spectrometer. Infrared spectra were collected on an IBM IR/32 FTIR spectrometer. Elemental analyses were performed by Schwartzkopf Microanalytical Laboratories.

A ^1H COSY (correlated spectroscopy) spectrum was obtained at 300.152 MHz, using a 16-step phase cycle to suppress axial peaks and artifacts from quadrature imbalance and to provide phase modulation in t_2. The spectral window of ±233 Hz was centered at δ 7.13. Resonances outside this window, from traces of water and undeuterated solvent, were suppressed by a 250-Hz four-pole Butterworth filter. A 90° pulse (8.0 μs) was used for both P_1 and P_2. Sixteen 512-point FID's (acquisition time of 0.550 s) were accumulated at each of 256 t_1 values (2 ms increment). The resulting symmetrical data matrix was treated by multiplying by a sine bell before Fourier transformation in each dimension. The data matrix was magnitude calculated after the second FT.

Synthesis of Chlorobis(tetraphenylcyclopentadienyl)titanium(III)–$^3/_2$-Tetrahydrofuran, I. Dry THF (75 mL) was added to a solid mixture of $TiCl_3$ (1.85 g, 12.0 mmol) and K-$(C_5HPh_4)\cdot{}^1/_2$ THF (11.18 g, 25.1 mmol). The reaction mixture was refluxed for several hours followed by solvent removal in vacuo. The green residue was extracted with benzene followed by evaporation of the extract to dryness under vacuum. The resulting solid was dissolved in a minimum of THF, and double the volume of pentane was layered on the solution. After several days the solution was filtered to give emerald green I (7.62 g, 8.2 mmol) in 68% yield. Anal. Calcd for $C_{128}H_{108}Cl_2O_3Ti_2$: C, 82.61; H, 5.85. Found: C, 82.48; H, 5.87.

Table I. Crystal and Refinement Data for I

formula	$C_{58}H_{42}TiCl\cdot CH_2Cl_2\cdot(C_4H_8O)_{1/2}$
crystal system	triclinic
space group	$P\bar{1}$
a, Å	12.878 (4)
b, Å	14.586 (5)
c, Å	15.888 (4)
α, deg	63.08 (2)
β, deg	79.10 (2)
γ, deg	63.67 (2)
V, Å^3	2385 (1)
Z	2
ρ(calcd), g cm^{-1}	1.31
temp, °C	23
μ, cm^{-1}	4.0
cryst dimens, mm	0.34 × 0.34 × 0.34
diffractometer	Nicolet R3m/μ
radiatn	graphite-monochromated Mo Kα (λ = 0.71073 Å)
scan technique	$\theta/2\theta$
2θ scan range, deg	$4 \le 2\theta \le 45$
data collected	$\pm h,\pm k,+l$
scan speed, deg/min	variable, 4–20
rflns collected	6561
unique data	6198
unique data, $(F_o) \ge 4\sigma(F_o)$	4281
R(int), %	1.54
std rflns	3 stds/197 rflns
decay	≤1% variation
R_F, %	6.13
R_{wF}, %	6.05
$\Delta(\rho)$, e Å^{-3}	0.58
mean shift/esd max	0.069
GOF	1.580
data/parameter	8.0
g[a]	0.0006

[a] $w^{-1} = \sigma^2(F_o) + g(F_o)^2$.

Synthesis of Dichlorobis(tetraphenylcyclopentadienyl)titanium(IV)–$^3/_2$-Tetrahydrofuran, II. Dry THF (75 mL) was added to a solid mixture of I (2.06 g, 2.2 mmol) and AgCl (0.48 g, 3.3 mmol). The solution was stirred overnight and filtered in air and the THF solvent removed by rotary evaporation. The magenta residue was dissolved in 35 mL of boiling toluene, and 5 mL of hexanes was added to the boiling solution. The solution was cooled to 5 °C overnight, to precipitate burgundy microcrystals of $(C_5HPh_4)_2TiCl_2$ (1.41 g, 1.6 mmol) in 73% yield. Recrystallization from THF/pentane yields II. Anal. Calcd for $C_{128}H_{108}Cl_4O_3Ti_2$: C, 79.58; H, 5.63. Found: C, 79.49; H, 5.38.

X-ray Diffraction Study of Chlorobis(tetraphenylcyclopentadienyl)titanium(III), I. Crystal data and the parameters used during the collection and refinement of diffraction data are summarized in Table I. A deep green crystal of $(C_5HPh_4)_2TiCl\cdot CH_2Cl_2\cdot(C_4H_8O)_{1/2}$, grown slowly from CH_2Cl_2/pentane, was attached to a fine glass fiber with epoxy cement. The compound was found to crystallize in the triclinic space group $P\bar{1}$. Unit-cell parameters were derived from the least-squares fit of the angular settings of 24 reflections with 18° < 2θ < 22°. No absorption correction was needed (regular crystal shape, μ = 4.0 cm^{-1}). A profile fitting procedure was applied to all intensity data to improve the precision of the measurement of weak reflections.

The Ti and Cl(1) atoms were found by heavy-atom methods. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses and were calculated and fixed in idealized positions (d(C–H) = 0.96 Å, with thermal parameters equal 1.2 times the isotropic equivalent of the carbon to which it is attached). The H(1) and H(6) atoms were located and refined isotropically. Phenyl rings were fit to rigid hexagons (d(C–C) =

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[3] Castellani, M. P.; Wright, J. M.; Geib, S. J.; Rheingold, A. L.; Trogler, W. C. *Organometallics* **1986**, *5*, 1116.

[4] Narula, S. P.; Sharma, H. K. *Inorg. Synth.* **1986**, *24*, 181.

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for I

	x	*y*	*z*	U^a
Ti	1541.0 (7)	780.7 (7)	1722.8 (6)	31.8 (5)
Cl(1)	436 (1)	2057 (1)	2363 (1)	57.5 (9)
C(1)	3481 (4)	−280 (4)	1522 (3)	34 (3)
C(2)	3439 (4)	−127 (4)	2341 (3)	35 (3)
C(3)	3170 (4)	1042 (4)	2044 (3)	34 (3)
C(4)	2988 (4)	1587 (4)	1048 (3)	32 (3)
C(5)	3210 (4)	759 (4)	711 (3)	32 (2)
C(6)	1291 (4)	−128 (4)	947 (3)	34 (3)
C(7)	1268 (4)	−835 (4)	1915 (3)	35 (3)
C(8)	238 (4)	−210 (4)	2284 (3)	32 (3)
C(9)	−363 (4)	854 (4)	1530 (3)	33 (3)
C(10)	324 (4)	907 (4)	697 (3)	32 (3)
C(21)	4471 (3)	−2114 (3)	3485 (2)	53 (3)
C(22)	4672	−2966	4400	72 (4)
C(23)	4057	−2728	5151	75 (4)
C(24)	3240	−1638	4987	67 (4)
C(25)	3039	−786	4072	49 (3)
C(26)	3655	−1024	3321	40 (3)
C(31)	2573 (2)	2646 (2)	2523 (2)	44 (3)
C(32)	2791	3102	3040	58 (4)
C(33)	3743	2468	3656	65 (4)
C(34)	4478	1378	3755	59 (4)
C(35)	4261	921	3238	45 (3)
C(36)	3308	1555	2622	39 (3)
C(41)	1667 (2)	3621 (3)	110 (2)	44 (3)
C(42)	1503	4741	−436	53 (3)
C(43)	2439	5041	−622	58 (3)
C(44)	3537	4221	−261	79 (4)
C(45)	3701	3101	285	62 (3)
C(46)	2765	2801	470	34 (3)
C(51)	3776 (3)	−97 (2)	−436 (2)	44 (3)
C(52)	3845	−21	−1351	49 (3)
C(53)	3421	1033	−2113	50 (3)
C(54)	2927	2010	−1960	55 (3)
C(55)	2857	1933	−1045	52 (3)
C(56)	3282	880	−283	36 (3)
C(71)	2159 (3)	−2672 (3)	3346 (2)	64 (3)
C(72)	2880	−3819	3730	83 (4)
C(73)	3530	−4338	3137	82 (4)
C(74)	3459	−3710	2161	89 (5)
C(75)	2738	−2563	1778	65 (4)
C(76)	2088	−2044	2370	39 (3)
C(81)	−1233 (3)	−837 (3)	3306 (2)	50 (3)
C(82)	−1747	−1202	4180	68 (4)
C(83)	−1303	−1329	4980	74 (4)
C(84)	−345	−1090	4906	68 (4)
C(85)	169	−725	4032	52 (3)
C(86)	−275	−599	3232	38 (3)
C(91)	−2305 (3)	2032 (3)	805 (2)	47 (3)
C(92)	−3484	2700	815	58 (4)
C(93)	−3945	2972	1581	61 (3)
C(94)	−3227	2578	2336	52 (3)
C(95)	−2049	1910	2325	42 (3)
C(96)	−1588	1637	1559	35 (3)
C(101)	−472 (3)	2968 (3)	−346 (3)	43 (3)
C(102)	−733	3861	−1241	59 (3)
C(103)	−462	3646	−2044	62 (4)
C(104)	70	2538	−1953	53 (3)
C(105)	331	1645	−1058	42 (3)
C(106)	60	1860	−255	33 (3)
$Cl(2)^b$	6653 (3)	5159 (2)	2998 (2)	175 (2)
$Cl(3)^b$	9095 (4)	4581 (5)	2997 (4)	211 (5)
$Cl(3')^b$	8708 (15)	4355 (20)	3816 (8)	176 (15)
$Cl(3'')^b$	8486 (16)	3655 (15)	3919 (9)	155 (12)
$C(dcm)^b$	8116 (13)	4015 (12)	3243 (12)	137 (12)
$C(dcm)'^b$	8071 (19)	4568 (28)	2811 (19)	163 (23)
$C(thf)(1)^b$	1016 (11)	4425 (8)	4861 (7)	183 (9)
$C(thf)(2)^b$	1884 (13)	3817 (8)	5425 (6)	175 (10)
$C(thf)(3)^b$	133 (14)	4322 (9)	5270 (7)	198 (11)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] These atoms form disordered molecules of CH_2Cl_2 and THF (see text).

Table III. Selected Bond Distances (Å) and Angles (deg) for I

	(a) Bond Distances		
Ti–Cl(1)	2.312 (2)	C(1)–H(1)	0.93 (4)
Ti–C(1)	2.335 (4)	C(2)–C(26)	1.487 (5)
Ti–C(2)	2.356 (5)	C(3)–C(36)	1.495 (8)
Ti–C(3)	2.469 (6)	C(4)–C(46)	1.496 (5)
Ti–C(4)	2.461 (5)	C(5)–C(56)	1.497 (6)
Ti–C(5)	2.426 (4)	C(6)–C(7)	1.415 (6)
Ti–C(6)	2.322 (7)	C(7)–C(8)	1.432 (6)
Ti–C(7)	2.410 (6)	C(8)–C(9)	1.429 (5)
Ti–C(8)	2.473 (6)	C(9)–C(10)	1.438 (6)
Ti–C(9)	2.477 (6)	C(10)–C(6)	1.401 (5)
Ti–C(10)	2.363 (6)	C(6)–H(6)	1.03 (3)
$Ti–Cnt(1)^a$	2.085 (5)	C(7)–C(76)	1.493 (5)
$Ti–Cnt(2)^a$	2.084 (6)	C(8)–C(86)	1.487 (5)
C(1)–C(2)	1.403 (8)	C(9)–C(96)	1.489 (5)
C(2)–C(3)	1.435 (7)	C(10)–C(106)	1.485 (4)
C(3)–C(4)	1.424 (6)		
C(4)–C(5)	1.431 (9)		
C(5)–C(1)	1.419 (5)		
	(b) Bond Angles		
Cl(1)–Ti–Cnt(1)	112.3 (2)	Cnt(1)–Ti–Cnt(2)	136.4 (2)
Cl(1)–Ti–Cnt(2)	111.3 (2)		

[a] Cnt(1) = ring centroid of C(1), C(2), C(3), C(4), C(5). Cnt(2) = ring centroid of C(6), C(7), C(8), C(9), C(10).

1.395 Å). The asymmetric unit contains one molecule of disordered CH_2Cl_2 that has three nearly colocated orientations of 66.7, 17.3, and 16.0% occupancy. Additionally, three peaks refined as carbon atoms, C(thf)(1) to C(thf)(3), are located near the inversion center and are believed to be half of a disordered THF molecule. Atomic coordinates are provided in Table II, selected bond distances and angles in Table III, and the least-squares planes and dihedral angles for the rings are provided in Table IV.

The final difference Fourier synthesis showed only a diffuse background (maximum contour 0.58 e $Å^{-3}$). An inspection of F_o vs. F_c values and trends based on sin θ, Miller index, or parity group failed to show any systematic errors. All computer programs used in the data collection and refinement are contained in the Nicolet (Madison, WI) program packages P3, SHELXTL (version 5.1), and XP.

Results and Discussion

Synthesis and Spectroscopic Characterization of I. Titanium trichloride and $K(C_5HPh_4)$ react in refluxing THF to produce chlorobis(tetraphenylcyclopentadienyl)titanium(III)-$^3/_2$-tetrahydrofuran, I, in 68% yield (eq 1).

$$TiCl_3 + 2K(C_5HPh_4) \xrightarrow[\Delta]{THF} (C_5HPh_4)_2TiCl + 2KCl \quad (1)$$

A ^1H NMR spectrum of decomposed I in benzene-d_6 solution confirmed the presence of lattice THF in crystals of I. Complex I dissolves readily in THF, dichloromethane, and benzene and is air-sensitive in solution as well as in the solid state. A cyclic voltammogram of I was obtained in THF solution with 0.25 M tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte at a scan rate of 200 mV/s. An irreversible oxidation ($E_{p_a} = 0.14$ V) and a partly reversible reduction ($E°' = -1.92$ V) were observed ($Cp_2Fe^{0/+}$, $E°' = 0.09$ V). The irreversibility of the oxidation may arise from instability of the $(C_5HPh_4)_2TiCl^+$ cation, since $(C_5HPh_4)_2TiCl_2$ can be isolated.

Chlorobis(tetraphenylcyclopentadienyl)titanium(III) was characterized by EPR spectroscopy under a variety of conditions (Table V). An EPR spectrum taken in benzene or toluene solution at 25 °C displayed a large signal at $g = 1.957$ with a line width of ca. 11 G and a less intense signal at $g = 1.979$ with a narrower line width of 2–3 G (Figure 1). Admission of air caused a decrease in the intensity of both resonances. In THF or dichloromethane

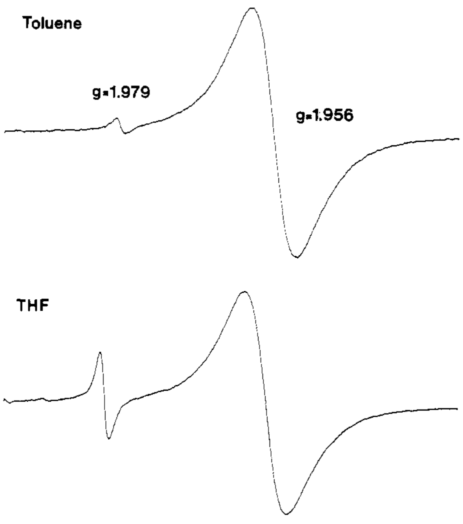

Figure 1. EPR spectra of $(C_5HPh_4)_2TiCl$ in toluene (top) and THF (bottom) solutions at room temperature.

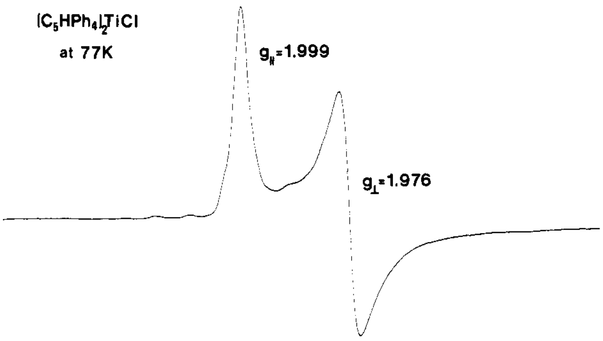

Figure 2. EPR spectrum of $(C_5HPh_4)_2TiCl$ in a toluene glass at 77 K.

solution both resonances remain, with the low-field resonance growing in relative intensity. Various $(C_5R_5)_2TiCl(L)$ systems (R = H,[5] Me,[6] L = see Table V) exhibit a g value of 1.968–1.980, while in $(C_5Me_5)_2TiCl$,[6] without a donor ligand, g = 1.956 ($(C_5H_5)_2TiCl$ exists as a dimer[7]). These values resemble those obtained for I and, when combined with the observed solvent effect, suggest that the high-field signal (g = 1.957) arises from I without an associated ligand while the low-field signal (g = 1.979) arises from I with an associated ligand. The EPR spectrum of I in a toluene glass at 77 K is displayed in Figure 2. The room-temperature signal splits into parallel ($g_\parallel$ = 1.999) and perpendicular ($g_\perp$ = 1.976) components. A THF or benzene glass of I at 77 K yields the same spectrum as does a toluene glass, suggesting that a similar species exists in all glasses. The weighted average of $g_\parallel$ and $g_\perp$ at 77 K equals 1.984, which is close to the g value of the signal assigned to the THF adduct (1.979) in the room-temperature solution spectrum. This suggests that cooling the solution forms more of the adduct. Evan's NMR method[8] magnetic moment determinations yielded different moments for benzene (μ_{eff} = 1.59 μ_B) and dichloromethane (μ_{eff} = 1.86 μ_B) solutions of I, which could arise from an interaction with solvent.

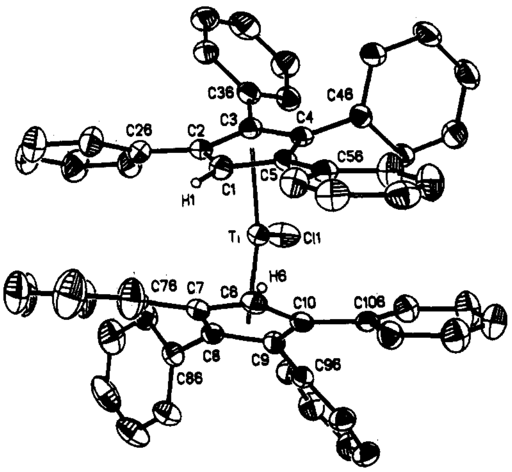

Figure 3. Thermal ellipsoid diagram (40% probability) and labeling scheme for $(C_5HPh_4)_2TiCl$.

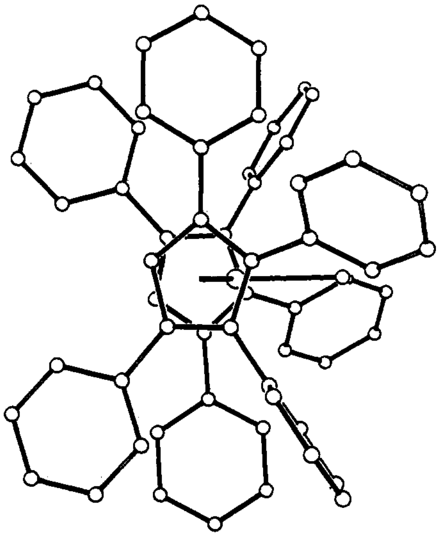

Figure 4. View of $(C_5HPh_4)_2TiCl$ showing the arrangement of the phenyl groups from above.

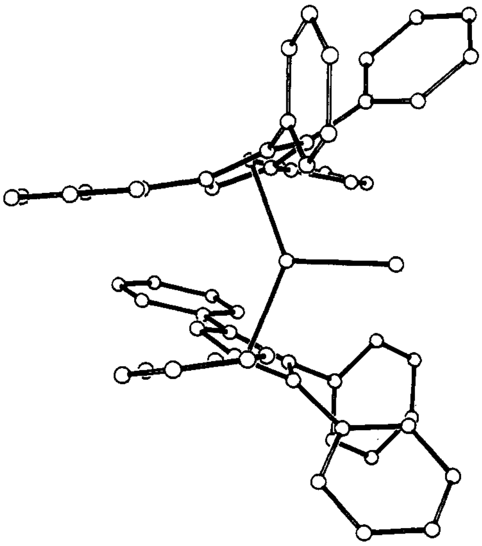

Figure 5. View of $(C_5HPh_4)_2TiCl$ showing the arrangement of the phenyl groups from the side.

Addition of a large excess (>100 equiv) of either pyridine or dimethylphenylphosphine to benzene solutions of I led to an increase in the intensity of the g = 1.979 resonance as compared to the high-field peak. It appears from this

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[5] Green, M. L. H.; Lucas, C. R. *J. Chem. Soc., Dalton Trans.* **1972**, 1000.

[6] de Boer, E. J. M.; Ten Cate, L. C.; Staring, A. G. J.; Teuben, J. H. *J. Organomet. Chem.* **1979**, *181*, 61.

[7] Jungst, R.; Sekutowski, D.; Davis, J.; Luly, M.; Stucky, G. *Inorg. Chem.* **1977**, *16*, 1645.

[8] Evans, D. F.; James, T. A. *J. Chem. Soc.*, Dalton *Trans.* **1979**, 723.

that further coordination takes place, but the presence of both resonances shows that even with stronger bases an equilibrium exists. Ammonia gas decomposes a benzene solution of I in minutes. In contrast, $(Cp_2TiCl)_2$ reacts with these donors to form stable adducts.[5] Complex I also fails to react with PhLi while $(Cp_2TiCl)_2$ does so rapidly.[9a]

Table IV. Least-Squares Planes for I

Plane I [C(1) to C(5)]:
$0.9693X + 0.2465Y - 0.0120Z - 4.2051 = 0$

atom	dev, Å	atom	dev, Å
C(1)[a]	0.0051	H(1)	0.0305
C(2)[a]	−0.0153	C(26)	−0.045
C(3)[a]	0.0199	C(36)	0.3408
C(4)[a]	−0.0170	C(46)	0.0950
C(5)[a]	0.0074	C(56)	0.1522

Plane II [C(21) to C(26)]:
$0.7103X + 0.5614Y + 0.4247Z - 5.6409 = 0$

Plane III [C(31) to C(36)]:
$0.5640X + 0.6493Y - 0.5102Z - 1.5171 = 0$

Plane IV [C(41) to C(46)]:
$-0.1939X + 0.0929Y + 0.9766Z - 3.0463 = 0$

Plane V [C(51) to C(56)]:
$0.8968X + 0.4322Y + 0.0944Z - 4.7120 = 0$

Plane VI [C(6) to C(10)]:
$0.5017X + 0.6452Y + 0.5762Z - 2.0742 = 0$

atom	dev, Å	atom	dev, Å
C(6)[a]	−0.0049	H(6)	−0.0665
C(7)[a]	−0.0037	C(76)	−0.1990
C(8)[a]	0.0108	C(86)	−0.1351
C(9)[a]	−0.0137	C(96)	−0.3210
C(10)[a]	0.0114	C(106)	0.0243

Plane VII [C(71) to C(76)]:
$0.7533X + 0.5685Y + 0.3306Z - 1.8845 = 0$

Plane VIII [C(81) to C(86)]:
$0.6087X - 0.7671Y - 0.2024Z + 0.4324 = 0$

Plane IX [C(91) to C(96)]:
$0.1854X + 0.9826Y - 0.0123Z - 0.9073 = 0$

Plane X [C(101) to C(106)]:
$0.8979X + 0.4078Y + 0.1657Z - 1.2005 = 0$

Dihedral Angles between Planes

	II	III	IV	V	VI
I	34.8	44.6	100.2	13.0	50.4
II		56.7	70.8	23.1	
III			123.2	42.4	
IV				92.4	

	VII	VIII	IX	X
VI	20.7	107.8	44.0	36.0
VII		92.5	46.0	15.6
VIII			129.7	78.5
IX				55.6

[a] Atoms used in plane calculation.

Table V. EPR Data for Chlorobis(cyclopentadienyl)titanium(III) Compounds

compd	solv	temp, K	*g* values	ref
$(C_5HPh_4)_2TiCl$	toluene	298	1.979, 1.957	this work
	THF	298	1.979, 1.957	
	toluene	77	1.999 (‖), 1.976 (⊥)	
	THF	77	1.999 (‖), 1.976 (⊥)	
$(C_5H_5)_2TiCl(L)$ L = py, PPh_2Me, $EtNH_2$	THF	213–293	1.980	5
$(C_5Me_5)_2TiCl$	toluene	*a*	1.956	6
$(C_5Me_5)_2TiCl(CO)$	toluene	*a*	1.968	6

[a] No temperature listed, presumably the spectrum was obtained at ambient temperature.

Table VI. Selected Bond Distances (Å) and Angles (deg) for I and Similar Compounds

compd	M–Cl	M–Cnt	Cnt(1)–M–Cnt(2)	ref
$(C_5HPh_4)_2TiCl$	2.312 (2)	2.085 (5)	136.4 (2)	this work
$Cp^*{}_2TiCl$	2.363 (1)	2.06 (2)	143.6	9b
$(Cp_2TiCl)_2$[a]	2.536 (2)	2.049	131.2	7
	2.558 (2)	2.058	133.4	
Cp_2VCl	2.390 (4)	1.946 (7)	139.5 (3)	12
$(C_5H_4Me)_2VCl_2$	2.398 (2)	1.991	133.4	11
Cp_2TiCl_2	2.364 (3)	2.058	131.0 (1)	10
$Cp^*{}_2TiCl_2$	2.352 (1)	2.127 (4)	137.4 (1)	*b*
	2.346 (1)	2.128 (4)		
$Cp^*CpTiCl_2$	2.3518 (2)	2.085	132	*c*

[a] The crystal studied possesses two crystallographically independent molecules. [b] McKenzie, T. C.; Sanner, R. D.; Bercaw, J. E. *J. Organomet. Chem.* **1975**, *102*, 457. [c] Rogers, R. D.; Benning, M. M.; Kurihara, L. K.; Moriarty, K. J.; Rausch, M. D. *Ibid.* **1985**, *293*, 51.

Molecular Structure. The structure of I (Figures 3–5) is the first of a bent metallocene containing the tetraphenylcyclopentadienyl ligand. Complex I crystallizes as well-separated molecules with a staggered C_5 ring configuration. The crystals of I used in this X-ray study were obtained from a dichloromethane/pentane solution, which yielded molecules of I with one associated dichloromethane and one-half of a THF molecule. Both solvent molecules were disordered. Selected bond distances and angles are provided in Table III and the least-squares planes and dihedral angles for the rings are provided in Table IV.

The two unsubstituted carbons of the two C_5 rings (C(1) and C(6)) are brought near each other by tilting the two rings. This minimizes steric interactions between the phenyl groups on opposing cyclopentadienyl rings. The chlorine atom lies 2.312 (2) Å from the titanium center, symmetrically placed between the C_5 rings on the plane containing the C_5 ring centroids and titanium atom. This Ti–Cl bond length is the shortest among several isoelectronic or isostructural compounds listed in Table VI, which includes the recently reported $Cp_2{}^*TiCl$.[9b] Steric crowding from a second chlorine atom probably accounts for longer M–Cl distances in Cp_2TiCl_2[10] and $(C_5H_4Me)_2VCl_2$[11] while additional electron density, located in an a_1 orbital (d_{z^2}) antibonding with respect to the M–Cl bond, lengthens that bond in Cp_2VCl. Complex I possesses the longest metal–C_5 centroid (M–Cnt) distances (2.085 Å) of the isostructural group. Shorter M–Cnt bonds in $(C_5H_4Me)_2VCl_2$ arise from the difference in the covalent radii[13] of Ti and V (0.09 Å) and from the oxidation state difference. In isostructural Cp_2VCl an additional electron located in an orbital bonding to the Cp rings shortens the M–Cnt distances even further.[7] This marked decrease in bond length may explain the anomalous large Cnt–M–Cnt angle in this complex.

The M–Cnt bonds in $(Cp_2TiCl)_2$ and Cp_2TiCl_2 are the same length, suggesting that steric interactions between the phenyl groups from opposing C_5 rings elongate the M–Cnt bonds in I. These steric repulsions also cause variations in the individual Ti–C bond lengths. The M–C bonds within each of the unsubstituted compounds in

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(9) a) Teuben, J. H.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1972**, *46*, 313. b) Pattiasina, J. W.; Heeres, H. J.; van Bolhuis, F.; Meetsma, A.; Teuben, J. H.; Spek, A. L. *Organometallics* **1987**, *6*, 1004.

(10) Clearfield, A.; Warner, D. K.; Saldarriaga-Molina, C. H.; Ropal, R.; Bernal, I. *Can. J. Chem.* **1975**, *53*, 1622.

(11) Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422.

(12) Fieselmann, B. F.; Stucky, G. D. *J. Organomet. Chem.* **1977**, *137*, 43.

(13) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, 1960.

Table VI vary by only 0.035–0.050 Å, whereas the Ti–C bonds in I differ by as much as 0.155 Å. Carbon atoms on phenyl rings 3, 4, 8, and 9, directed inside the sandwich, tilt away from the chlorine atom (and each other) to create a pocket for it.

As expected, the proximity of the phenyl groups in this system causes them to bend out of the C_5 plane away from the titanium center (deviations listed in Table IV). In particular the ipso carbon atoms of rings 3 and 9, which lie directly over the chlorine atom, move far out of the C_5 plane (ca. 0.33 Å). Steric interactions between phenyl groups force a small opening of the Cnt(1)–M–Cnt(2) angle of I (136.4°) as compared to most other compounds listed in Table VI (130–133°) and prevent dimerization of I. It is noteworthy that the Cnt(1)–M–Cnt(2) angle in $Cp_2{}^*TiCl$ (143.6°) exceeds that in I. This can be attributed to the near proximity of the unsubstituted cyclopentadienyl carbons in I, which allows a more acute interring angle than in $Cp_2{}^*TiCl$. This increased ring–ring repulsion should also be present in $Cp_2{}^*TiCl_2$ and helps rationalize the long M–Cnt distances (Table VI) found in this complex.

Synthesis of II. Reaction of I with AgCl under nitrogen in THF produces air-stable dichlorobis(tetraphenylcyclopentadienyl)titanium(IV)-$^3/_2$-tetrahydrofuran in 73% yield according to eq 2. Direct reaction between $TiCl_4$ and

$$(C_5HPh_4)_2TiCl + AgCl \xrightarrow{THF} (C_5HPh_4)_2TiCl_2 + Ag^0 \qquad (2)$$

$K(C_5HPh_4)$ did not yield II, and only a brown, intractable solid formed. Similarly, the reaction between $TiCl_4$ and $Na(C_5Me_5)$ produced only low yields of $(C_5Me_5)_2TiCl_2$ and was attributed to steric hindrance of the bulky ligand and concomitant reduction of $TiCl_4$ by $Na(C_5Me_5)$.[14] Oxidation of $(C_5Me_5)_2TiCl$ with aqueous HCl yields the desired product. Oxidizing I with silver chloride[15] simplifies product purification and produces air-stable II in good yields. Compound II dissolves in THF, dichloromethane, benzene, and toluene. Solutions of II in benzene or toluene decompose slowly over several days, while solutions in the more polar solvents THF and dichloromethane remain stable for at least a week. The reaction between II and $AgNO_3$ in THF/H_2O solution results in slow precipitation (days) of AgCl, in contrast to the rapid reaction between Cp_2TiCl_2 and $AgNO_3$ in THF/H_2O solution.

Solution Structure of II. The phenyl rings of $(C_5HPh_4)_2Fe$ rotate rapidly on the NMR time scale at room temperature.[3] As the temperature drops, however, the ortho and meta resonances of the more crowded, inner phenyl rings each split into two new absorptions as those phenyl rings stop spinning. No evidence was found[3] for slowed rotation of the cyclopentadienyl rings down to −95°. The bent structure of II causes greater interaction between the phenyl groups of opposing C_5 rings than in $(C_5HPh_4)_2Fe$. This increase in contact might raise the barrier to phenyl ring rotation, and therefore we examined the ^1H NMR spectra of II at several temperatures.

The room-temperature ^1H NMR spectrum of II in toluene-d_8 solvent (Figure 6) consists of two doublets, a triplet, a quartet, and a triplet with relative areas of 2:3:2:2:2. A ^1H COSY spectrum of II (Figure 6) shows the quartet to be two overlapping triplets. Peak integrations and previous work[3] with $(C_5HPh_4)_2Fe$ suggest that the doublets (a, x) be assigned to the ortho protons, the overlapping triplets (c, z) to the para protons, and the remaining triplets (b, y) to the meta protons. The ^1H COSY spectrum supports these assignments and shows multiplets a, b, and c couple to each other as do multiplets x, y, and z. These assignments imply the phenyl groups rotate rapidly on the NMR time scale at room temperature. We assign the cyclopentadienyl proton resonance for II, s, to the peak on the downfield side of doublet x (7.03 ppm). A ^2H NMR of II (isotopically enriched with ^2H at the cyclopentadienyl position) displays a broad resonance at ca. 6.9 ppm, confirming that this absorption shifts into the aromatic region of the spectrum. Peak integrations, peak widths, and the absence of spin coupling also require that singlet s be assigned to the cyclopentadienyl ring proton. This resonance occurs ca. 1.1 ppm downfield of the ^1H resonance in Cp_2TiCl_2 (5.88 ppm).[16] A similar difference (ca. 1.8 ppm) exists between the ring proton in $(C_5HPh_4)_2Fe$ (5.90 ppm)[3] and those in Cp_2Fe (4.11 ppm),[17] and probably arises from additional deshielding of the tetraphenylcyclopentadienyl proton from two adjacent phenyl rings. Variable-temperature NMR experiments (vida infra) support these assignments and suggest that multiplets a, b, and c arise from phenyl rings 3, 4, 8, and 9 while multiplets x, y, and z arise from phenyl rings 2, 5, 7, and 10 (Table VII).

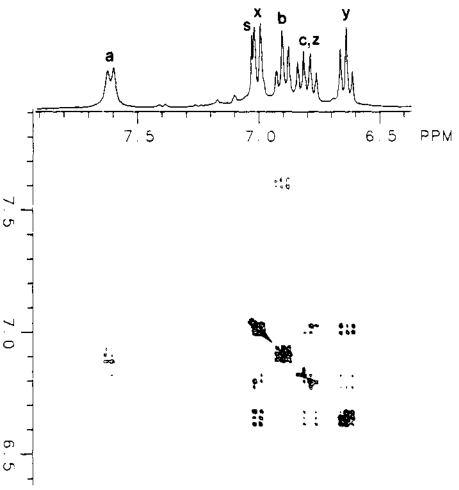

Figure 6. 2-D COSY ^1H NMR spectrum of $(C_5HPh_4)_2TiCl_2$ in toluene-d_8 solvent at room temperature.

The ^1H NMR spectra of II, obtained between 40 and −90 °C, are displayed in Figure 7. The changes observed in this series of spectra resemble those observed for $(C_5HPh_4)_2Fe$.[3] Doublet a (ortho protons) rapidly collapses into the base line, and between −60 and −90 °C two new resonances appear. Each of these resonances (6.19 and 8.94 ppm) integrates to one proton centered about the position of doublet a in the 40 °C spectrum. Similarly, triplet b (meta protons) disappears around −60 °C and two new absorptions grow in centered about it (6.52 and 7.27 ppm) between −80 and −90 °C. Because these spectra resemble those obtained for $(C_5HPh_4)_2Fe$,[3] we propose the same model to account for this fluxional behavior. At 40 °C, all phenyl groups rotate rapidly on the NMR time scale. As the solution cools, the rate of rotation slows, especially for the more crowded phenyl rings 3 and 4. At low temperatures these rings stop rotating and align roughly perpendicular to the C_5 plane. Thus one side of the phenyl

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(14) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219.

(15) Silver chloride oxidizes Cp_2V and Cp_2VCl to Cp_2VCl and Cp_2VCl_2, respectively. Gladyshev, E. N.; Boyushkin, P. Ya.; Cherkasov, V. K.; Sokolov, V. S. *Isv. Akad. Nauk SSR, Ser. Khim.* **1979**, 1444.

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Table VII. ^{1}H NMR Spectral Data for II[a]

resonance	phenyl rings[b]	proton type	position, ppm
a	3, 4, 8, and 9	ortho	7.61
s		cyclopentadienyl	7.03
x	2, 5, 7, and 10	ortho	7.00
b	3, 4, 8, and 9	meta	6.90
c	3, 4, 8, and 9	para	6.81
z	2, 5, 7, and 10	para	6.79
y	2, 5, 7, and 10	meta	6.64

[a] In toluene-d_8 (100%) at 20 °C. [b] Based on the numbering scheme used in Figure 1, where C(36) denoted ipso carbon of ring 3, C(46) for ring 4, etc.

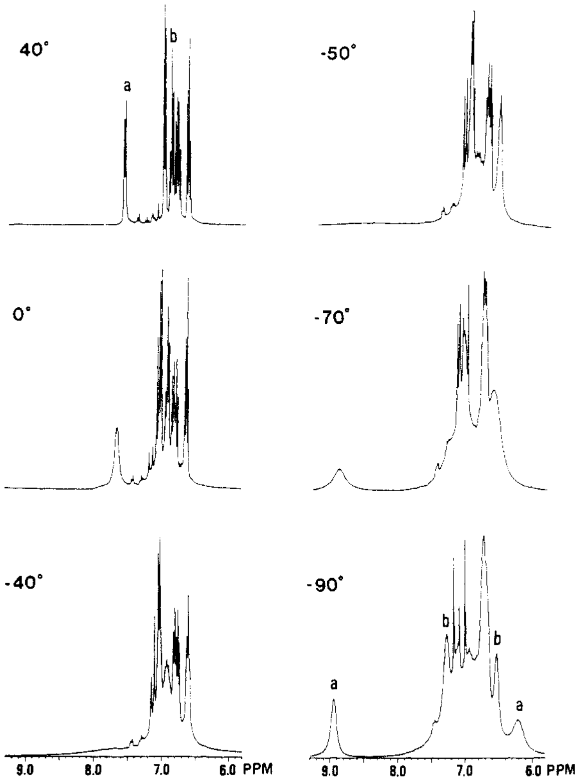

Figure 7. Temperature (°C) dependence of the ^{1}H NMR spectrum of $(C_5HPh_4)_2TiCl_2$.

ring remains inside the sandwich and the other outside. In II, the inside ortho proton probably points directly at the titanium center, which may account for the anomalous broadness of the upfield ortho resonance at -90 °C. Phenyl rings 2 and 5 can still rotate because of the small substituent on C(1); however, they should finally become coplanar with the C_5 ring as found in the solid-state structures of several bis(tetraphenylcyclopentadienyl)metal complexes (e.g. Figure 1). An interesting difference between this system and $(C_5HPh_4)_2Fe$ is that singlet s moves downfield only ca. 0.2 ppm (vs 0.55 ppm) and stays a sharp singlet. No evidence is observed for slowed C_5 rotation above -95 °C.

From the spectra in Figure 7 the rate of phenyl ring rotation and the free energy of activation at the coalescence temperature for doublet a and triplet b can be estimated.[18] A peak separation of 825 Hz at -90 °C generates a ring rotation rate of 1800 Hz at coalescence (ca. -45 °C) for the ortho protons, a (eq 3). The meta protons, b, yield a peak separation of 225 Hz at -90 °C producing a rate of ring rotation of 500 Hz at -62 °C.

$$k_c = (\pi/\sqrt{2})(\Delta\nu) \qquad (3)$$

From the peak separations the free energy of activation can be estimated (eq 4) to be

$$\Delta G_c^{\ddagger} = (4.575 \times 10^{-3})T[9.972 + \log (T/\Delta\nu)] \qquad (4)$$

9.8 ± 0.2 kcal/mol for the ortho protons and 9.6 ± 0.5 kcal/mol for the meta protons at coalescence. These values are the same (within experimental error) as the free energy of activation determined[3] for $(C_6HPh_4)_2Fe$ (9 ± 1 kcal/mol). This suggests that the motions of the phenyl groups of each C_5 ring are independent of those on the other ring even in the bent metallocene geometry.

Chemical Reduction of I. Decamethyltitanocene has been prepared and its chemistry extensively studied;[14,19] however, no structural data are available for the parent metallocene. The much reduced reactivity of octaphenylmetallocenes[2] as compared to that of the unsubstituted metallocenes and decamethylmetallocenes led us to explore the possibility of isolating octaphenyltitanocene. All reductions were carried out under an argon atmosphere in THF solution unless stated otherwise.

The reaction between $TiCl_2$ and $K(C_5HPh_4)$ at 20 °C or higher temperatures resulted in the exclusive formation of $(C_5HPh_4)_2TiCl$. No reaction occurs at -78 °C, probably because of the low solubility of $TiCl_2$. Reacting $K(C_5HPh_4)$ and $TiCl_2$ (prepared in situ by the reduction of $TiCl_4$ with Mg) at -78 °C rapidly generated I as the product.[20] An attempt to prepare $(C_5HPh_4)_2Ti$ by the method used for the C_5Me_5 derivative[14] did not succeed. Methyllithium reduced solutions of II at -78 °C or room temperature to compound I.

The reduction of I was also investigated as a method to prepare $(C_5HPh_4)_2Ti$. Solutions of I fail to react with solid alkali metals (Na or K) at room temperature and decompose at elevated temperatures. Solutions of I stirred over Na/K alloy at room temperature decompose slowly. Dropwise addition of a sodium naphthalide (NaNp) solution to solutions of I in THF did not reach an endpoint even after addition of 2 equiv of NaNp. After the rapid addition (ca. 2 s) of 1.0 equiv of NaNp the solution turns from emerald green to green-brown. Within 24 h this solution decomposes. Replacing the argon atmosphere with CO (as long as 3 h later) yields a solution whose IR spectrum displays two CO stretches (1966 and 1892 cm^{-1}) that coincide with those for $Cp_2Ti(CO)_2$ (1965 and 1885 cm^{-1}).[21] This species does not lose CO under vacuum. The formation of $(C_5HPh_4)_2Ti(CO)_2$ suggests that $(C_5HPh_4)_2Ti$ (III) may exist in solution. The ability of solutions of I to consume more than 1 equiv of NaNp suggests, however, that $(C_5HPh_4)_2Ti$ is not the only species produced. The NaNp reduction of I under an H_2 atmosphere also yields a dark brown solution. Removing the H_2 under vacuum causes the solution to turn green-brown; readmitting H_2 causes the dark brown color to reappear. Unfortunately, no Ti–H stretches were observed in the IR spectrum and the incomplete reduction of paramagnetic I prevented further investigation by NMR spectroscopy.

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Organometallics **1987**, *6*, 2531–2536

for a research fellowship. We thank P. Moeller for experimental assistance and for helpful discussions regarding the NMR studies.

Registry No. I, 110614-69-2; II, 110614-70-5; $Cp_2Ti(CO)_2$, 12129-51-0; $K(C_5HPh_4)$, 58081-04-2; $TiCl_3$, 7705-07-9; chlorobis(tetraphenylpentadienyl)titanium(III), 110614-68-1.

Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic thermal parameters, and H-atom coordinates (6 pages); a listing of structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

Neighboring Group Participation in Organometallic Chemistry: Anchimeric Assistance in Catalyzed Arene Exchange Reactions of (Diarylalkane)tricarbonylchromium Complexes

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Nucleophilic catalysis of the migration of a tricarbonylchromium group from one ring to the other in diarylalkane tricarbonyl derivatives has been observed and compared with catalysis of external exchange. Internal catalysis by a neighboring tricarbonylchromium is also being reported. These results demonstrate the intermediacy of a chromium complex having three carbonyl groups, ketone, and two η^2-bound arenes. The consequences of this result for metal exchange reactions are discussed.

Introduction

The study of solvent effects in systems involving neighboring group participation has provided important information regarding reaction mechanisms and transition-state geometries, particularly in systems involving direct solvent participation.[1] In arene exchange reactions of (arene)tricarbonylchromium complexes, the addition of nucleophiles such as ketones, ethers, and nitriles enhances the rate of arene exchange by orders of magnitude. This also leads to a change in mechanism of the reaction from one which is first order in both complex and attacking arene to one which is first order in complex and nucleophile and independent of attacking arene.[2] We have proposed a single mechanism for both of these processes involving either rate-limiting attack of arene or nucleophile followed by rapid collapse to product.[2a]

As a further extension of our earlier work on neighboring group assistance in the arene exchange reactions of a series of (diarylalkane)tricarbonylchromium complexes, we report the effect of the addition of ketones and ethers on the rates, mechanism, and degree of internal arene participation in these systems. Such an investigation provides information regarding the existence of species of the types $(\eta^4\text{-arene})Cr(CO)_3L$, $(\eta^2\text{-arene})Cr(CO)_3L_2$, or $L_3Cr(CO)_3$ (L = nucleophile) prior to trapping by arene, through reactivity selectivity relationships involving internal vs. external arene exchange.

Catalysis can also be accomplished by a second mole of (arene)tricarbonylchromium complex. Mechanisms proposed for this reaction include an S_N2 displacement from a sandwich-like structure of two complexes,[3] use of a bound carbonyl ligand as a nucleophile,[2a,c] and formation of a bridging carbonyl complex.[4] This process has been investigated by using bis(tricarbonylchromium) adducts of the same diarylalkanes to address these possible pathways, which should have different geometrical requirements for catalysis.

Table I. Internal (k_i) and External (k_e) Arene Exchange Rate Constants for the Reaction of (1,3-Diphenylpropane)tricarbonylchromium (6) in C_6H_6/C_6D_{12} Mixtures Catalyzed by Acetone-d_6 or Dioxane-d_8 at 170 °C[a] Along with NGP Values[b]

cat.	$[C_6H_6]$, M	$10^7k_i^{obsd}$, s^{-1}	$10^7k_e^{obsd}$, s^{-1}	NGP, M
none	11.3	3.1 ± 0.3	5.7 ± 0.3	6
acetone-d_6, 0.05 M	1.0	24.7 ± 1.3	19.2 ± 1.9	1.6
acetone-d_6, 0.05 M	2.8	9.5 ± 0.5	28.3 ± 2.3	0.8
acetone-d_6, 0.05 M	5.6		28.0 ± 2.2	
acetone-d_6, 0.5 M	2.8		289 ± 9	
acetone-d_6, 0.5 M	5.6		349 ± 20	
dioxane-d_8, 4.0 M	1.0		313 ± 21	
dioxane-d_8, 4.0 M	2.8		332 ± 55	
dioxane-d_8, 4.0 M	5.6		371 ± 26	

[a] 0.2 M complex [b] Calculated according to eq 5–7.

Table II. Rates of Internal (k_i) and External (k_e) Arene Exchange Reactions of (Di-*p*-tolylmethane)tricarbonylchromium (5) Catalyzed by Acetone-d_6 or THF-d_8 at 170 °C[a] Along with NGP Values[b]

cat.	$10^7k_i^{obsd}$, s^{-1}	$10^7k_e^{obsd}$, s^{-1}	NGP, M
none	63.5 ± 4.2	5.7 ± 0.3	126
acetone-d_6, 0.2 M	146 ± 8	103 ± 5	9
acetone-d_6, 0.5 M	248 ± 10	336 ± 23	6
acetone-d_6, 1.0 M	488 ± 18	840 ± 24	6
THF-d_8, 0.2 M	99.5 ± 2.1	83.3 ± 1.6	5
THF-d_8, 0.5 M	110 ± 4	149 ± 2	3
THF-d_8, 1.0 M	167 ± 9	371 ± 18	3

[a] 0.2 M complex in neat C_6D_6. [b] Calculated as in Table I.

Experimental Section

General Data. All solvents were purified by published procedures.[5] Cyclohexane-d_{12}, benzene-d_6, acetone-d_6, dioxane-d_8,

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