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An Investigation of the Reaction of Bis(cyclopentadienyl)titanium Dichlorides with Trimethylaluminum. Mechanism of an α-Hydrogen Abstraction Reaction[†]

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The reaction of Me_3Al with Cp_2TiCl_2 and its derivatives has been studied. Synthetic procedures for the preparation of $(C_5R_5)(C_5H_5)TiCl_2$ from $(C_5R_5)Li$ and $(C_5H_5)TiCl_3$ were developed, and sources of the major byproducts $(C_5H_5)_2TiCl_2$ and $(C_5R_5)_2TiCl_2$ are suggested. The derivatives studied were (C_5R_5) = $C_5H_4SiMe_3$, 1,2,4-trimethylcyclopentadienyl, $(CH_3)_5C_5$, indenyl, 1,3-$Ph_2C_5H_3$, and $(CH_3)C_5H_4$. All of these complexes reacted with 1 equiv of $(CH_3)_3Al$ to produce $Cp_2Ti(CH_3)Cl\cdot Al(CH_3)_2Cl$ which would react further with a second equivalent of $(CH_3)_3Al$ to yield a $Cp_2TiCH_2AlMe_2Cl$ derivative. The isotope effect for the parent reaction was 2.9. Substituents on the ring slowed the rate of methylene formation. A mechanism for α-hydrogen abstraction from a Ti–$(CH_3)Cl$ unit by an aluminum alkyl is proposed in which the Lewis acidic aluminum alkyl activates the titanium methyl group by complexation with the chlorine. The resulting aluminate then serves as a strong Lewis base to abstract the α-hydrogen.

Introduction

Since Ziegler's discovery[1,2] that ethylene could be polymerized at low temperature and pressure to a high molecular weight polymer using a catalyst formed from the reaction of an early transition-metal halide, such as $TiCl_4$ and aluminum alkyls, there has been a keen interest in the nature of the interaction of the aluminum alkyls with the transition-metal center and its ligands. The insolubility of catalysts derived from $TiCl_4$ has made mechanistic studies difficult and has led to a large effort to synthesize soluble polymerization catalysts.[3]

One such soluble catalyst for the polymerization of ethylene is the system $Cp_2TiCl_2/AlR_{3-n}X_n$ (n = 0, 1, 2; R = alkyl, X = halide).[4] This catalyst system has become the best characterized (in terms of the kinetics of polymerization and subsequent side reactions)[3a] of those studied.

In the mid-1960's several groups studied the reaction of Cp_2TiCl_2 with $AlMe_3$ and noticed that methane was evolved and that the organometallic product contained Ti–CH_2–Al units.[5] Tebbe and Parshall[6] reinvestigated this system and purified the titanium methylene complex $Cp_2Ti\text{–}CH_2AlMe_2Cl$ (1) and other derivatives.

Tebbe's methylene compound demonstrated olefin metathesis activity and reacted with internal acetylenes to produce the titanacyclobutenes $Cp_2TiCRCR'CH_2$.[7] Tebbe also demonstrated that 1 was very reactive with organic carbonyl compounds, transferring a methylene unit to ketones[6] and esters to produce olefins and vinyl ethers, respectively. This aluminum-stabilized methylene derivative showed similar chemistry to the tantalum alkylidene complex prepared by Schrock.[8] Tebbe also showed that 1 reacted with propylene to form isobutylene. As part of a reinvestigation of this methanation reaction with unsymmetrical (mixed-ring) analogues of 1, it was discovered that 1 reacted with monosubstituted olefins under certain conditions to cleanly produce titanacyclobutanes.[9] These titanacyclobutanes derived from 1 have been shown to be well-defined olefin metathesis catalysts[10] and have been utilized in organic synthesis.[11a,b]

This study was initiated to provide information regarding the interaction of aluminum alkyls with a transition-metal center and lend insight into the α-H abstraction involved in formation of 1 from Cp_2TiCl_2 and $AlMe_3$. Such mechanistic information would prove valuable in developing better synthetic procedures for 1, extending the synthesis to the formation of higher alkylidene units and understanding the generation of catalysts in olefin polymerization and metathesis systems.

Results

Preparation of the "Mixed-Ring" Titanocene Dichlorides. The "mixed-ring" titanocene dichlorides (i.e., those compounds having one substituted and one nonsubstituted cyclopentadienyl ligand) were prepared by reaction of $CpTiCl_3$ with the lithium salt of a substituted

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[†] Contribution No. 6714.

(1) Ziegler, K.; Holzkamp, E.; Breil, H.; Martin. H. *Angew. Chem.* **1955**, *67*, 541.

(2) For an extensive review of Ziegler-Natta polymerization, see: Boor, J., Jr. "Ziegler-Natta Catalysts and Polymerizations"; Academic Press: New York, 1979. See also: Pino, P.; Mulhaupt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 857.

(3) (a) See Boor,[2] pp 115–120. (b) Ballard, D. G. H. *Adv. Catal.* **1973**, *23*, 263. (c) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99. (d) Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357.

(4) Natta, G.; Dino, P.; Mazzanti, G.; Giannini, U. *J. Inorg. Nucl. Chem.* **1958**, *8*, 612. Breslow, D. S.; Newburg, N. R. *J. Am. Chem. Soc.* **1957**, *79*, 5073. Breslow, D. S.; Newburg, N. R. *Ibid.* **1959**, *81*, 81. See also ref 31, pp 397–415 for chemistry related to the Cp_2Ti–Al system.

(5) See ref 3c, pp 136–137. Heins, E.; Hinck, H.; Kaminsky, W.; Oppermann, G.; Paulinat, P.; Sinn, H. *Makromol. Chem.* **1970**, *134*, 1. Feay, D. C.; Fujioka, G. S. "Abstracts of Papers", Tenth International Conference on Coordination Chemistry, Tokyo, 1967; p 1.

(6) (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Klabunde, U.; Tebbe, F. N.; Parshall, G. W.; Harlow, R. L *J. Mol. Catal.* **1980**, *8*, 37.

(7) Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074. Tebbe, F. N.; Harlow, R. L. *Ibid.* **1980**, *102*, 6151. McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbaugh T. S.; Tebbe, F. N. *Ibid.* **1981**, *103*, 5584.

(8) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

(9) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876. Lee, J. B., et al. *Ibid.* **1981**, *103*, 7358.

(10) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491.

(11) (a) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270. (b) Grubbs, R. H.; Straus, D. A.; Stille, J.; Ho, S. C.; Hentges, S. G. "Abstracts of Papers", 183rd National Meeting of the American Chemical Society, Las Vegas, NV, 1982; American Chemical Society: Washington, D.C., 1982; Abst 13. *Chem. Eng. News* **1982**, April 19, pp 34–35.

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Table I. NMR Spectral Data for Titanocene Methylene Compounds in C_6D_6

compd		chem shift,[a] δ
$Cp_2\overline{TiCH_2AlMe_2Cl}$ (1)	^1H	8.28 (s, CH_2) 5.67 (s, C_5H_5) −0.28 (br s, $AlMe_2$)
	^{13}C	188 (CH_2) 114 (C_5H_5)
$Cp'Cp\overline{TiCH_2AlMe_2Cl}$ (8)	^1H	8.12 (ABq, J = 6.9 Hz, CH_2) 5.78, 5.39 (m, C_5H_4Me) 5.66 (s, C_5H_5) 1.66 (s, C_5H_4Me) −0.32, −0.36 (2s, br, $AlMe_2$)
$Cp^{tms}Cp\overline{TiCH_2AlMe_2Cl}$ (9)		8.47, 8.24 (2d, J = 6.5 Hz, CH_2) 6.7 (m, $C_5H_4Me_3Si$) 5.72 (s, C_5H_5) 0.01 (s, $C_5H_4Me_3Si$) −0.28, −0.32 (2s, br, $AlMe_2$)
<Cp>$Cp\overline{TiCH_2AlMe_2Cl}$ (10)	^1H	7.99, 7.54 (2d, J = 6.8 Hz, CH_2) 5.47, 5.13 (2d, J = 0.6 Hz, 1,2,4-$C_5H_2Me_3$) 5.72 (s, C_5H_5) 1.76, 1.63, 1.46 (3s, 1,2,4-$C_5H_2Me_3$)
	^{13}C	180.6 (CH_2) 112.9 (C_5H_5) 16.3, 14.2 ($C_5Me_3H_2$)
[Cp]$Cp\overline{TiCH_2AlMe_2Cl}$ (11)		7.2–6.8 (m, 1,3-$C_5H_3Ph_2$) 6.4–6.1 (m, 1,3-$C_5H_3Ph_2$) 5.62 (s, C_5H_5) 8.23 (ABq, J = 0.5 Hz, CH_2) 0.27 (s, br, $AlMe_2$)
$Cp^*Cp\overline{TiCH_2AlMe_2Cl}$ (12)	^1H	7.57, 6.94 (2d, J = 7.3 Hz, CH_2) 5.66 (s, C_5H_5) 1.59 (s, C_5Me_5) −0.19, −0.36 (2s, br, $AlMe_2$)
	^{13}C	173.9 (J = 125 Hz, CH_2) 113.6 (C_5H_5) 121.8 (C_5Me_5) 12.6 (C_5Me_5)

[a] Shifts relative to C_6D_5H at δ 7.15. ^{13}C shifts relative to C_6D_6 at δ 128.0.

cyclopentadienide. The mixed-ring compounds prepared were (Cp^{tms})CpTiCl$_2$ (Cp^{tms} = $C_5H_4SiMe_3$; **2**), Ind(Cp)TiCl$_2$ (Ind = indenyl; **3**), ⟨Cp⟩CpTiCl$_2$ (⟨Cp⟩ = 1,2,4-trimethylcyclopentadienyl; **4**), [Cp]CpTiCl$_2$ ([Cp] = 1,3-diphenylcyclopentadienyl; **5**), Cp*CpTiCl$_2$ (Cp* = C_5Me_5; **6**), and Cp′CpTiCl$_2$ (Cp′ = C_5H_4Me; **7**). Compound **6** was prepared by reaction of Cp*TiCl$_3$ with CpLi. An attempt was made to prepare (1,2,4-triphenylcyclopentadienyl)-CpTiCl$_2$. This compound proved unstable to hydrolysis during workup and could not be isolated in pure form.

In many of these preparations, not only was the anticipated mixed-ring compound observed, but also Cp_2TiCl_2 and often $\bar{C}p_2TiCl_2$ ($\bar{C}p$ = substituted Cp). For example, the prepartion of Cp′CpTiCl$_2$ often resulted in a statistical mixture of Cp_2TiCl_2, Cp′CpTiCl$_2$, and Cp′$_2$TiCl$_2$. This problem was partially circumvented by slow addition of an ether slurry of Cp′Li to a cold ether solution of CpTiCl$_3$. At best, the crude reaction mixtures contained at least 10% Cp_2TiCl_2 (commercial $(MeC_5H_5)_2$ contains approximately 4% $(C_5H_6)_2$),[12] which could be fractionally crystallized from Cp′CpTiCl$_2$. Typically, the synthesis of other mixed-ring compounds resulted in formation of less than 10% Cp_2TiCl_2. In one preparation of Cp*CpTiCl$_2$ from Cp*TiCl$_3$ and CpLi, the ratio of Cp*CpTiCl$_2$ to Cp*$_2$TiCl$_2$ was approximately 2:1. Fractional crystallization provided pure Cp*CpTiCl$_2$.

Preparation of the Mixed-Ring Methylenes. Reaction of toluene solutions of the mixed-ring titanocene dichlorides with more than 2 equiv of AlMe$_3$ resulted in the formation of analogues of **1** (eq 1). The reactions pro-

$$Cp\bar{C}pTiCl_2 + 2AlMe_3 \rightarrow Cp\bar{C}p\overline{TiCH_2AlMe_2Cl} + AlMe_2Cl + CH_4 \quad (1)$$

$\bar{C}p$ = a substituted cyclopentadienyl

ceeded in poor to moderate yields for the mixed-ring compounds with the exception of Ind(Cp)TiCl$_2$. ^1H NMR spectroscopy of the reaction of Ind(Cp)TiCl$_2$ with AlMe$_3$ indicated extensive decomposition had occurred, although there were resonances in the δ 7–8 region, indicative of formation of Ti–CH$_2$–Al species. With the exception of $Cp'Cp\overline{TiCH_2AlMe_2Cl}$ (**8**) and $[Cp]Cp\overline{TiCH_2AlMe_2Cl}$ (**11**), the titanium methylene compounds were oils which crystallized only slowly, if at all. If allowed to stand undisturbed in a drybox, both $\langle Cp\rangle Cp\overline{TiCH_2AlMe_2Cl}$ (**10**) and $Cp^*Cp\overline{TiCH_2AlMe_2Cl}$ (**12**)[9] crystallized over a period of several weeks. ^1H NMR spectral data are listed in Table I.

Reaction of Cp_2TiCl_2, $Cp_2TiMeCl$, and Cp_2TiMe_2 with AlMe$_3$ and AlMe$_2$Cl. Reactions were followed by ^1H NMR spectroscopy. Due to their lability, the aluminum alkyl adducts of the titanium species could not be isolated.

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(12) Reynolds, L. T.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1959**, *9*, 86.

Table II. ^1H NMR Spectral Parameters for Methyltitanium and Aluminum Mixtures

	Cp reson, δ	Ti-Me reson,[a] δ
$Cp_2TiMeCl$	5.81	0.82
Cp_2TiMe_2	5.67	0.06
Cp_2TiCl_2 + $1AlMe_3$	5.79	0.94
$Cp_2TiMeCl$ + $AlMe_2Cl$	5.79	0.94
$Cp_2TiMeCl$ + $2AlMe_3$	5.73	0.90
Cp_2TiCl_2 + $2AlMe_3$	5.79	0.92

[a] Spectra recorded in C_6D_6; referenced to C_6D_5H, δ 7.15.

Table III. Kinetics Data for the Reaction $Cp_2TiCl_2 + 4AlMe_3 \longrightarrow 1 + AlMe_2Cl + CH_4$ at 53 °C

$[TiMeCl{\cdot}Al]_{t=0}$	$[AlMe_3]_{t=0}$	10^4k_{obsd}, $M^{-1}\ s^{-1}$	solv
0.2	1.4	1.6 ± 0.5	C_6D_6
0.1	0.7	1.8	C_6D_6
0.2	0.7	2.3 ± 0.3	C_6D_6
0.2	0.6	3.4	CD_2Cl_2

Table IV. Activation Parameters for the Reaction $Cp_2TiCl_2 + 4AlMe_3 \longrightarrow 1 + AlMe_2Cl + CH_4$[a]

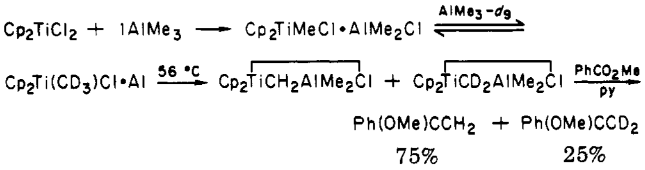
T, °C	$10\,k_{obsd}$
38	7.7×10^{-5}
57	3.3×10^{-4}
72	1.1×10^{-3}

[a] $\Delta H^{\ddagger} = 16 \pm 0.2$ kcal·mol^{-1}; $\Delta S^{\ddagger} = -26 \pm 1$ eu; $\Delta G^{\ddagger}_{330} = 25 \pm 1$ kcal·mol^{-1}.

Table V. Observed Rates of the Reaction $\overline{\mathrm{Cp}}\mathrm{CpTiCl_2} + 4\mathrm{AlMe_3} \longrightarrow \overline{\mathrm{Cp}}\mathrm{CpTiCH_2AlMe_2Cl} + \mathrm{AlMe_2Cl} + \mathrm{CH_4}$ at 53 °C in C_6D_6

compd	10^5k_{obsd}, $M^{-1}\ s^{-1}$
Cp_2TiCl_2	23
$\underline{\mathrm{Cp}}^{tms}\mathrm{CpTiCl_2}$	8
Cp'_2TiCl_2	7
[Cp]$CpTiCl_2$	12
<Cp>$CpTiCl_2$	3
Cp*$CpTiCl_2$	1
Cp_2TiBr_2	17 (measd at 57.5 °C)

Scheme I



^1H NMR data for the reaction products described below appear in Table II.

One equivalent of $AlMe_3$ reacts rapidly with Cp_2TiCl_2 to form $Cp_2TiMeCl{\cdot}AlMe_{3-n}Cl_n$, as shown by the appearance of a new Cp resonance at δ 5.79 (10 H) and a methyl resonance at δ 0.91 (3 H). An identical spectrum was obtained when 1 equiv of $AlMe_2Cl$ was allowed to react with $Cp_2TiMeCl$. Heating these solutions to 56 °C for 19 h resulted in the formation of a 30% yield of a 6:1 mixture of $Cp_2\mathrm{TiCH_2AlMeClCl}$ and 1. Further heating resulted in formation of a homogeneous blue-green solution which exhibited a broad ^1H NMR spectrum.

Reaction of 1.21 equiv $AlMe_3$ with $Cp_2TiMeCl$ resulted in formation of a mixture of 78% CpTiMeCl·Al (·Al designates $AlMe_{3-n}Cl_n$) and 22% $CpTiMe_2$. Similarly, when 1.19 equiv of $AlMe_2Cl$ was allowed to react with Cp_2TiMe_2, a mixture of 87% $Cp_2TiMeCl{\cdot}Al$ and 13% Cp_2TiMe_2 was observed, the ratio $[Cp_2TiMe_2][AlMe_2Cl]/[Cp_2TiMeCl][AlMe_3]$ was 0.06 for both solutions.[13] When these solutions were heated to 65 °C for 6 h, an 80% yield of 1 was formed by way of eq 2 and 3.

$$Cp_2TiMeCl{\cdot}AlMe_3 \rightleftharpoons Cp_2TiMe_2 + AlMe_2Cl \qquad (2)$$

$$Cp_2TiMeCl{\cdot}AlMe_3 \rightarrow 1 + CH_4 \qquad (3)$$

Reaction of Cp_2TiCl_2 with greater than 2 equiv of $AlMe_3$ resulted in formation of $Cp_2TiMeCl{\cdot}Al$. Heating these solutions to 65 °C resulted in the formation of 1 according to eq 1 at the same rate at which the reaction of Cp_2TiMe_2 with $AlMe_2Cl$ proceeds.

The reaction of Cp_2TiCl_2 with 1 equiv of $AlMe_3$ followed by 1 equiv of $AlMe_3$-d_9 gave rise to a ^1H NMR spectrum which indicated that $Cp_2Ti(CH_3)Cl{\cdot}Al$ and $Cp_2Ti(CD_3)Cl{\cdot}Al$ were present in a 1:1 ratio Scheme I. This solution was heated to 56 °C, and the extent of reaction was monitored by ^1H NMR spectroscopy. As the reaction progressed, 1 was preferentially formed relative to 1-d_2 in a ratio of 2.9:1. The sample was quenched with methyl benzoate and pyridine[11] to produce 1-methoxy-1-phenylethylene-d_0 and -d_2 in a ratio of 2.9 ± 0.1:1, indicating the reaction proceeded with a moderate primary deuterium isotope effect.[14] Close examination of the vinylic AB quartet inicated that no 1-OMe-1-PhC═CHD was formed and demonstrated that only Ti–$CH_2(CD_2)$–Al groups and no Ti–CHD–Al groups were present upon reaction with methyl benzoate in the presence of pyridine.

Examination of the Kinetics of Titanium–Methylene Formation. Kinetics data for the reaction of Cp_2TiCl_2 with greater than 2 equiv of $AlMe_3$ in C_6D_6 at 53 °C were obtained by using varying concentrations of Cp_2TiCl_2 and $AlMe_3$. The reaction exhibited second-order kinetics and fit the rate law (eq 4). Second-order plots

$$-d(Cp_2TiMeCl{\cdot}Al)/dt = k_{obsd}(AlMe_3)(Cp_2TiMeCl{\cdot}Al) \qquad (4)$$

were linear over more than 2 half-lives.[15] Selected kinetics data are listed in Table III. An increase of 40–50% in k_{obsd} was observed when CD_2Cl_2 was employed as solvent. Activation parameters were derived from kinetics data obtained at 38, 57, and 72 °C and are listed in Table IV.

Kinetics data were also obtained for certain mixed-ring compounds[16] and are listed in Table V. The data for Cp_2TiCl_2, Cp'_2TiCl_2, and Cp_2TiBr_2 are included for comparison. An attempt was made to examine the reaction of Cp_2TiF_2 with greater than 2 equiv of $AlMe_3$; however,

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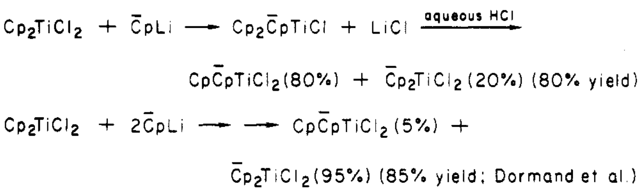
[13] This "equilibrium ratio" is not intended to represent an equilibrium constant. This ratio was calculated to indicate that the species formed from both reactions were present in approximately equal concentrations. An equilibrium constant would be difficult to estimate due to the complex equilibria involving all of the aluminum compounds.

[14] Tebbe,[6a] has observed that although Al–Me exchange is rapid between 1 and Al–Me_3-d_9, deuterium is not incorporated into the methylene unit of 1.

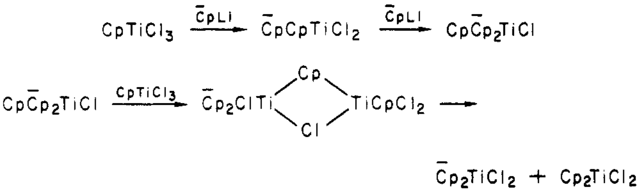
[15] After 2 half-lives, some of the solutions, particularly those with high concentrations of $AlMe_3$, began to show slight curvature. This is probably due to a competing reaction described by Sinn and Kaminsky.[3c] Product 1 can apparently react with the excess $AlMe_3$ or with another molecule of 1 producing poly-$TiCH_2Al$ species. These species can be formed by allowing 1 to stand with excess $AlMe_3$ or in neat $AlMe_3$. After long reaction times, red, toluene-insoluble solids can be isolated which have high reactivity towards acetone forming isobutylene or with DMAP in the presence of olefins yielding titanocyclobutanes. Ott, K. C.; Grubbs, R. H., unpublished results.

[16] Kinetics were not attempted on $IndCpTiCl_2$ due to decomposition; $Cp'CpTiCl_2$ was excluded due to the inability to obtain this material free from Cp_2TiCl_2.

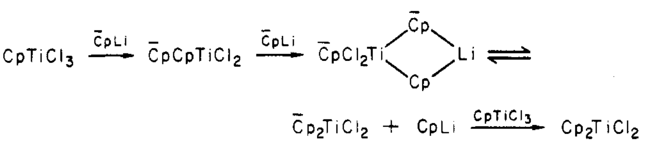
Scheme II



Scheme III



Scheme IV



this reaction proceeds rapidly to produce Cp_2TiMe_2 which is then converted to at least 40% $Cp_2\overline{TiCH_2AlMe_2F}$ in 1 h at 65 °C. Further heating converts this material into $Cp_2\overline{TiCH_2AlFMeF}$ and other unidentified products. Monitoring of the reaction by ^1H NMR spectroscopy proved unsuitable for kinetics analysis due to overlapped resonances.

Discussion

Synthesis of the Titanocene Dichlorides. As mentioned above, synthesis of mixed-ring titanocene dichlorides often resulted in production of Cp_2TiCl_2 and $\bar{C}p_2TiCl_2$ ($\bar{C}p$ = substituted Cp) as significant by-products. Dormond et al.[17] reported that ring exchange occurs when Cp_2TiCl_2 is reacted with 1 or 2 equiv of $Li\bar{C}p$; hydrolysis of the reaction mixtures with aqueous HCl gave good yields of $Cp\bar{C}pTiCl_2$ and $\bar{C}p_2TiCl_2$, respectively. It was suggested that the sterically smaller and less electron-donating Cp ligand is selectively hydrolyzed from the metal center (Scheme II). They do not mention the observation of any Cp_2TiCl_2 in the reaction mixture, and Scheme II is unable to account for the formation of Cp_2TiCl_2 which was observed in this work. An alternative explanation for the ring exchange via a bridging Cp intermediate is outlined in Scheme III. Such a ring exchange may occur in the reaction of Cp_2TiCl_2 and $TiCl_4$[18] (eq 5) but must have a

$$Cp_2TiCl_2 + TiCl_4 \xrightarrow[\text{reflux}]{\text{xylene}} 2CpTiCl_3 \qquad (5)$$

higher activation energy than for the reaction of $CpTiCl_3$ with $\bar{C}pLi$ which undergoes apparent ring exchange at or below room temperature.[19] The possibility also exists that the ring exchange proceeds through a Cp bridging a titanium and a $Li\bar{C}p$ as depicted in Scheme IV. The ability of such lithium alkyls to form aggregates is well-known.[20]

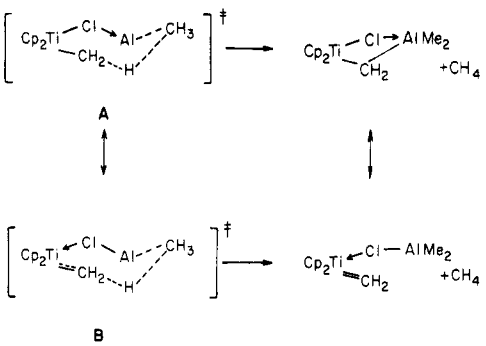
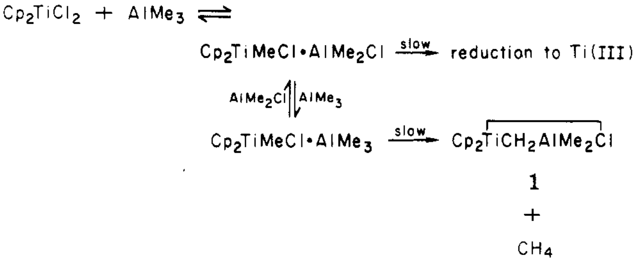


Figure 1.

Scheme V



Tuli et al.[21] report that the reaction of $CpTiCl_3$ and $Cp'Tl$ proceeds to yield $Cp'CpTiCl_2$ in greater than 85% yield. Thallium alkyls may be less prone to aggregation[22] and therefore are less likely to undergo ring exchange similar to that proposed in Scheme IV. However, $\bar{C}pTl$ is also not as reactive as the lithium analogues and may react more slowly with $Cp\bar{C}pTiCl_2$ to yield the species $Cp\bar{C}p_2TiCl$, thereby reducing the possibility of ring exchange via this complex.

Reaction of Cp_2TiCl_2, $Cp_2TiMeCl$, and Cp_2TiMe_2 with Aluminum Alkyls. Reaction of Cp_2TiCl_2 with 1 equiv of $AlMe_3$ proceeds rapidly to yield a solution having the stoichiometry $Cp_2TiMeCl·AlMe_2Cl$. The aluminum is assumed to form a weak complex with the chlorine on titanium.[23] $Cp_2TiMeCl$ can be released from the complex by removing the aluminum alkyl from solution by distillation or by the addition of Lewis bases such as ether. Additionally, the exchange of Al–Me and Ti–Me groups is facile on the chemical time scale as is indicated by the rapid exchange of $Cp_2TiMeCl·Al$ with $AlMe_3$-d_9. There is not a measurable isotope effect on this exchange reaction.

Addition of 1 equiv of $AlMe_3$ to $Cp_2TiMeCl·AlMe_2Cl$ produces only slight changes in the ^1H NMR spectrum, and $Cp_2\overline{TiCH_2AlMe_2Cl}$ (1) is slowly formed along with methane and $AlMe_2Cl$.

The results of these reactions are summarized in Scheme V, which indicates that one $AlMe_3$ methylates Cp_2TiCl_2. If no additional $AlMe_3$ is added to this mixture, only small amounts of titanium methylene compounds are slowly formed, and after long reaction times there is apparent

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(17) Dormond, A.; Ou-Khan; Tirouflet, J. *C. R. Acad. Sci. Ser. C* **1974**.

(18) (a) Gorsich, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 4744. (b) Gorsich, R. D. *Ibid.* **1960**, *82*, 4211. See also ref 34.

(19) Vitz and Brubaker have shown that ring exchange occurs photochemically: Vitz, E.; Brubaker, D. H. *J. Organomet. Chem.* **1974**, *82*, C16.

(20) Brown, T. L. *Adv. Organomet. Chem.* **1965**, *3*, 365.

(21) Tuli, R. K.; Chandra, K.; Sharma, R. K.; Kumar, N.; Gang, B. S. *Transition Met. Chem.* (*Weinheim, Ger.*) **1980**, *5*, 49.

(22) Lee, A. G. "The Chemistry of Thallium"; Elsevier: London, 1971.

(23) Kinetics for complexation and alkylation have been extensively studied for the $Cp_2TiCl_2/AlEt_2Cl$ system. Sosnovskaja[24] has shown that for the reaction $Cp_2TiCl_2 + AlEt_2Cl \rightleftharpoons Cp_2TiClEtAlEt_2Cl$ $K = 140\ M^{-1}$. Fink[25] has shown that the forward rate of reaction $Cp_2TiEtCl + AlEtCl_2 \rightleftharpoons Cp_2TiEtCl·AlEtCl_2$ is diffusion controlled and that the equilibrium constant $K = 5 \times 10^{-3}$–5×10^{-4} at 240 K.

(24) Sosnovskaja, L. N.; Fushman, E. A.; Borisova, L. F.; Shupik, A. N. *J. Mol. Catal.* **1980**, *9*, 411.

(25) Fink G.; Rotter, R.; Schnell, D.; Zoller, W. *J. Appl. Polym. Sci.* **1976**, *20*, 2779. Fink, G.; Rottler, R.; Kreiter, C. G. *Angew. Makromol. Chem.* **1981**, *96*, 1.

formation of a Ti(III) species.[26] When one additional equivalent of $AlMe_3$ is added, it is proposed that $AlMe_3$–$AlMe_2Cl$ exchange occurs producing an equilibrium concentration of $Cp_2TiMeCl\cdot AlMe_3$, which then in a slow step extrudes CH_4 forming 1, in accord with the observed second-order kinetics. Complex 1 is also produced from the reaction of either Cp_2TiMe_2 with $AlMe_2Cl$ or $Cp_2TiMeCl$ with $AlMe_3$. These two reactions proceed at the same rate as Cp_2TiCl_2 with $2AlMe_3$. This suggests that the necessary stoichiometry for formation of 1 is $Cp_2TiMeCl\cdot AlMe_3$ and that all of the above species are in equilibrium.

The Ti–Al species have been described as 1:1 adducts, primarily for simplicity of presentation. It should be noted, however, that due to the tendency of aluminum methyl and chloroaluminum ethyl compounds to form dimers, the formation of 1:2 Ti·Al adducts cannot be ruled out. Unquestionably, the product is formed from an aluminum adduct of $Cp_2TiMeCl$. The key question is the mode of transfer of the hydrogen from the Ti–CH_3.

The observations of a deuterium isotope effect k_H/k_D = 2.9 and a large, negative activation entropy of approximately −26 eu are consistent with the cyclic transition states depicted in Figure 1. Polarization of the Ti–Cl bond by aluminum as in the resonance structure B would be expected to increase the basicity of the Al–CH_3 bonds and concommitantly increase the acidity of the $TiCH_3$ α-hydrogens. Extrusion of CH_4 would then lead to the observed product 1.

The 50% increase in k_{obsd} when the solvent is changed from C_6D_6 to CD_2Cl_2, a solvent of higher dielectric constant,[28] is also consistent with an increase in dipole moment in the transition state depicted in Figure 1. Further support for this working model will be given later.

On the basis of "hard-soft" considerations,[29] an aluminum center should polarize a Ti–Br bond less than a Ti–Cl bond. If resonance structure B in Figure 1 is important, then reaction of Cp_2TiBr_2 with 2 equiv of $AlMe_3$ should proceed relatively slowly to $Cp_2\overline{TiCH_2AlMe_2Br}$, and in fact, under indentical conditions, Cp_2TiBr_2 is converted to $Cp_2\overline{TiCH_2AlMe_2Br}$ at 35–40% of the rate at which 1 is formed. Due to experimental difficulties, the rate at which Cp_2TiF_2 reacts with $AlMe_3$ to produce the corresponding titanium methylene compound could not be determined accurately. That the aluminum halide bond polarization in these reactions is important is indicated by the very rapid formation of Cp_2TiMe_2 and $AlMe_2F$ from the reaction of Cp_2TiF_2 with 4 equiv of $AlMe_3$. Apparently, the position of equilibrium of eq 6 lies in the center for X =

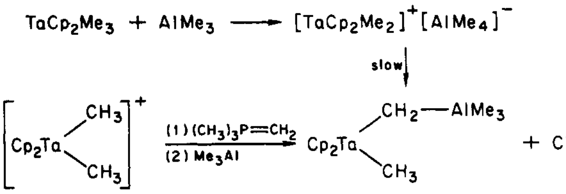
$$Cp_2TiX_2 + 2AlMe_3 \rightleftharpoons Cp_2TiMeX\cdot Al \rightleftharpoons Cp_2TiMe_2 + 2AlMe_2X \quad (6)$$

Cl and Br but far to the right for X = F. The subsequent reaction of Cp_2TiMe_2 with $AlMe_2F$ proceeds to a titanium methylene complex at at least the same rate as observed for the Cp_2TiCl_2 reaction.

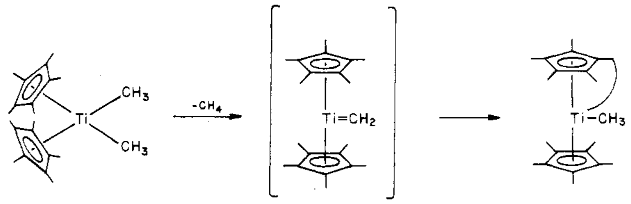
In an attempt to investigate the effect of larger and more electron-donating or accepting ligands on the rate of the titanium methylene formation reation, the mixed-ring compounds were synthesized and the kinetics of their reaction with $AlMe_3$ measured. These data are tabulated in Table V and appear in order of increasing size of the substituted cyclopentadienyl ligand. With the exception of [Cp], k_{obsd} varies inversely with the steric bulk and also with the relative donor ability[30] of the substituted cyclopentadienyl ligand. [Cp] can be considered to be a relatively electron-withdrawing ligand in comparison to the other ligands. Thus, there appear to be two trends demonstrated in the rate data for the mixed-ring compounds. One is that a dramatic decrease in k_{obsd} is seen with increasing steric bulk of the ligand, and the second being a decrease in k_{obsd} with increasing donor strength of the ligand. A better donor ligand would tend to decrease the Lewis acidity of the titanium center in structure B (Figure 1) and concommitantly decrease the acidity of the Ti–Me hydrogens. One might speculate that $IndCpTiCl_2$ would react with excess $AlMe_3$ to generate the analogous titanium methylene at a rate approximately equal to that of Cp_2TiCl_2. Unfortunately, $IndCpTiCl_2$ does not react cleanly with $AlMe_3$. This is perhaps related to the relative ease with which the η^5-indenyl ligand can "slip" to η^3-indenyl.

Related studies that are important in understanding this reaction are the reactions of $(Cp_2Ta(CH_3)_2)^{+}$[31] with bases and the thermolysis of $(C_5Me_5)_2Ti(CH_3)_2$.[32]

In the tantalum case it was demonstrated that $AlMe_4^-$ could serve as the base for removal of a proton from one of the methyl groups (eq 7). Methane and the $AlMe_3$ adduct of the tantalum methylene complex resulted from this reaction.[31] All the evidence suggests that this reaction proceeds by an α-hydrogen abstraction. The isotope effect is 3.4 ± 0.3. Thermolysis of $(C_5Me_5)_2Ti(CH_3)_2$ yielded the fulvene complex and methane in an intramolecular elimination reaction (eq 8).[32] Although the mechanism of this reaction is more difficult to define, the authors favored an α-H abstraction mechanism over an α-elimination scheme. The isotope effect for this reaction was 2.9.



(7)



(8)

In the more complex system under study, the distinction must be drawn between the direct abstraction of an α-hydrogen from the methyl group by an aluminate or the elimination of a hydrogen that has migrated to the metal from the methyl (eq 9).

The carbene hydride formed by the α-elimination process is unusual. Formally, the metal center is d^0 and as

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[26] Reduction of Cp_2TiCl_2 with $AlEt_3$ is rapid, producing $0.5C_2H_4$ and $0.5C_2H_6$ and the blue-green $Cp_2TiClAlEt_2Cl$: see ref 3c, pp 131, 136. Natta, G.; Mazzanti, F. *Tetrahedron* **1960**, *8*, 86. Heating $Cp_2TiMeCl\cdot AlMeCl_2$ yields a blue-green paramagnetic complex.[37]

[27] Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1980**, *102*, 7667.

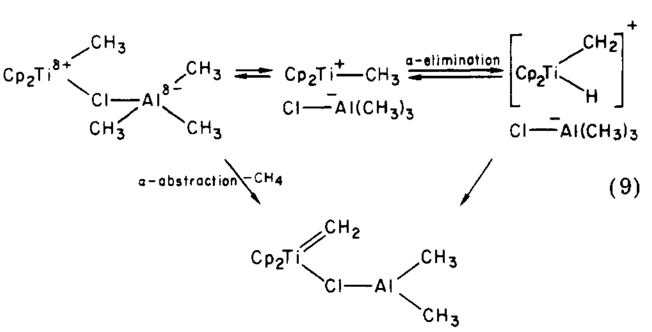
[28] ϵ: CH_2Cl_2, 9.08; C_6H_6, 2.28 "Handbook of Chemistry and Physics", 59th ed.; CRC Press: Cleveland, OH, 1979.

[29] Pearson, R. G. "Hard and Soft Acids and Bases"; Wiley: New York, 1973. Ho, T.-L. "Hard and Soft Acids and Bases Principle in Organic Chemistry"; Academic Press: New York, 1977.

[30] See: Calabro, D. C.; Hubbard, J. L.; Blevins, C. H.; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6839 and references therein.

[31] Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

[32] McDade, C.; Cram, Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629.



(9)

such the carbene must serve as a σ-donor without supporting back-donation. Although complete transfer is not required,[33] all of the results to date suggest this represents a high energy situation. This analysis, combined with the similarity of this reaction to those discussed above, supports the α-abstraction mechanism. The six-center reaction depicted in Figure 1 is consistent with all of the results. Other reactions which may proceed via similar six-center mechanisms as described above are the "ene" reaction[34] and the protonolysis of trialkylborons with carboxylic acids.[35] Both of these reactions proceed with deuterium isotope effects of approximately 3, and the "ene" reaction exhibits activation entropies of −30 to −40 eu, similar to that reported here (−26 eu). Although one-electron processes are not ruled out, it appears that processes leading to Ti(III) complexes are irreversible.

In summary, it is proposed that the reaction of Cp_2TiCl_2 with 2 equiv of $AlMe_3$ proceeds to an intermediate $Cp_2TiMeCl{\cdot}Al$ which goes on to produce 1 via an intramolecular attack of a strong base (Al–Me) on the activated α-hydrogen of the titanium methyl group. The aluminum serves as a strong Lewis acid to activate the titanium alkyl by complexing with the chlorine on Ti. After complexation the aluminum alkyl becomes a strong base. This ability to play a dual role is probably the reason for the unique role of aluminum alkyls in many catalytic systems.

Experimental Section

General Considerations. All manipulations of air- and/or moisture-sensitive compounds were performed by using glovebox and standard high vacuum or Schlenk line techniques. Argon used in Schlenk work was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4 Å molecular sieves. Diethyl ether, C_6D_6 (Merck, Sharp and Dohme), toluene, tetrahydrofuran, and hexane were dried and deoxygenated by stirring over CaH_2, degassed and were vacuum transferred onto purple sodium–benzophenone ketyl. Solvents for Schlenk work were vacuum transferred from sodium–benzophenone ketyl solutions into dry vessels equipped with Teflon needle valve closures and stored under Ar. CD_2Cl_2 was dried over CaH_2 and deoxygenated by several freeze–pump–thaw cycles. Solvents used for recrystallization of the titanocene dichlorides were used as received.

Trimethylaluminum (Alfa), dimethylaluminum chloride (Texas Alkyls), and $AlMe_3$ (2 M in toluene, Aldrich) were used as received. Cp_2TiCl_2 (Strem or Boulder Scientific) was purified by Soxhlet extraction with dichloromethane. This material was then recrystallized from toluene for the kinetics studies. $TiCl_4$ (Alfa) was used as received. Methylcyclopentadiene and cyclopentadiene dimers and indene were purchased from Aldrich. $AlMe_3$-d_9,[36] $Cp_2TiMeCl$,[37] Cp_2TiMe_2,[37] Cp_2TiBr_2,[38] HCp^{tms},[39] HCp^*,[40] H⟨Cp⟩,[41] and H[Cp][42] were prepared by literature methods. Lithium *tert*-butoxide was prepared from the reaction of *t*-BuOH with *n*-BuLi followed by sublimation.

Lithium cyclopentadienides (except Li[Cp]), were prepared by dissolving the cyclopentadiene in degassed *n*-hexane followed by slow addition of 1.1 equiv of 1.6 M *n*-BuLi/hexane (Aldrich). Li[Cp] was prepared by reaction of a benzene solution of H[Cp] with 1.1 equiv of *n*-BuLi/hexane. The lithium cyclopentadienide suspensions thus prepared were transferred under Ar onto a medium frit via cannula, washed repeatedly with *n*-hexane, and dried under high vacuum. $CpTiCl_3$[18] and Cp^*TiCl_3[43] were prepared by literature methods and purified by sublimation.

^1H NMR spectra were recorded on a Varian EM-390 or a JEOL FX-90Q. Probe temperatures were calculated by measuring $\Delta\nu$(MeOH).[44] Chemical shifts are referenced from residual protiosolvent resonances.

Preparation of $(C_5H_4(CH_3))CpTiCl_2$ (7). Several syntheses of this compound appear in the literature.[17,18b] Due to the irreproducibility of these preparations, the following preparation is included here.

A suspension of methylcyclopentadienyllithium (0.86 g, 10 mmol) in ether (20 mL) was slowly added dropwise via cannula to a stirred solution of $CpTiCl_3$ (2.193 g, 10 mmol) in 30 mL of ether at 0 °C under Ar. The bright yellow solution slowly deposited a red microcrystalline powder. After the addition was complete, the mixture was allowed to warm to room temperature. Stirring was continued for 30 min before approximately half of the ether was removed in vacuo, and 20 mL of 9 M aqueous HCl was added. The red solids were filtered and washed with 9 M aqueous HCl until the washings were colorless. The solids were washed several times with cold ether and dried to yield 2.1–2.4 g (80–90%) of a mixture of $Cp'CpTiCl_2$ which typically contained 10–20% of both Cp_2TiCl_2 and Cp'_2TiCl_2. Fractional crystallization of this mixture from hot toluene yielded 60–70% $Cp'CpTiCl_2$ as red needles which contained approximately 5–10% Cp_2TiCl_2. Performing the reaction at room temperature or with a 50% excess of Cp′Li results in near statistical mixtures of Cp_2TiCl_2, $Cp'CpTiCl_2$, and Cp'_2TiCl_2. ^1H NMR ($CDCl_3$) δ 6.54 (s, Cp), 6.73 (m, C_5H_4Me), 2.33 (s, C_5H_4Me).

Preparation of $(C_5H_4(CH_3))_2TiCl_2$. A slurry of LiCp′ (8.7 g, 101 mmol) in ether was slowly added to an ether solution of $TiCl_4$ (5.5 mL, 50 mmol) under Ar at 0 °C. The solution was stirred for 30 min and worked up as for **2**. The resulting solids were recrystallized from hot toluene to yield Cp'_2TiCl_2 (8.3 g, 60%). This material contained ca. 7% Cp_2TiCl_2 (and probably a larger amount of **7**). A small amount of this material was recrystallized from toluene and then chloroform to yield a material which contained no Cp_2TiCl_2; mp 215–219 °C dec (lit.[13] mp 217–218 °C dec). This material probably contained a small amount of **7**: ^1H NMR ($CDCl_3$) δ 6.30 (m, C_5H_4Me), 2.27 (s, C_5H_4Me).

Preparation of [(Trimethylsilyl)cyclopentadienyl]$CpTiCl_2$ (2). A solution of $Cp^{tms}Li$ (1.24 g, 8.6 mmol) in 10 mL of THF was slowly added via cannula to a solution of $CpTiCl_3$ (1.89 g, 8.6 mmol) in 10 mL of THF under an Ar atmosphere at room temperature. After the addition was complete, the red solution was stirred for 30 min. The solvent was removed in vacuo to leave a pinkish orange powder. The solids were scraped onto a frit and

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(33) Brookhardt, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(34) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556.

(35) Toporcer, L. H.; Dessy, R. E.; Green, S. I. E. *J. Am. Chem. Soc.* **1965**, *87*, 1236.

(36) $AlMe_3$-d_9 was prepared by reaction of $HgMe_2$-d_6 with Al powder in refluxing toluene. Hg-Me_2-d_6 was prepared from CD_3MgI and $HgCl_2$. Mole, T.; Jefferey, E. A. "Organoaluminum Compounds"; Elsevier: Amsterdam, 1972. Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556.

(37) Clauss, K.; Bestian, H. *Justus Liebigs Ann. Chem.* **1962**, *654*, 8. Topocer, L. H.; Dessy, R. E.; Green, S. I. E. *J. Am. Chem. Soc.* **1965**, *87*, 1236.

(38) Druce, P. M.; Kingston, B. M.; Lappert, M. F.; Spalding, T. R.; Srivastava, R. C. *J. Chem. Soc. A* **1969**, 2106.

(39) Cardoso, A.; Clark, R. J. H.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1156.

(40) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1.

(41) Conia, J.-M.; Leriverend, M.-L. *Bull. Soc. Chem. Fr.* **1970**, 2981. Ronganayakulu, K.; Sorenson, T. S. *Can. J. Chem.* **1972**, *50*, 3534.

(42) Drake, N. L.; Adams, J. Rr. *J. Am. Chem. Soc.* **1939**, *61*, 1326.

(43) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219. Only 1 equiv of LiCp* per $TiCl_3{\cdot}THF$ was used. Anhydrous HCl was used to convert the $Cp^*_2TiCl_2$ to Cp^*TiCl_3.

(44) Gordon, A. J.; Ford, R. A. "The Chemists Companion"; Wiley-Interscience: New York, 1972; p 303.

(45) Nesmeyanov, A. N. *J. Organomet. Chem.* **1973**, *57*, 55. The crystal structure of $Cp^*CpTiCl_2$ is reported without synthetic details.

washed with 6 M aqueous HCl until the washings were colorless. The solids were then washed with 2 × 5 mL of ethanol and 2 × 5 mL of ether. The red powder was recrystallized from hot $CHCl_3$/hexane to yield 2.1 g (76%) of deep red needles. No Cp_2TiCl_2 was observed by ^1H NMR: ^1H NMR ($CDCl_3$) δ 6.54 (s, Cp), 6.78, 6.57 (2t, J = 2 Hz, $C_5H_4Me_3Si$), 0.32 (s, $C_5H_4Me_3Si$).

Preparation of (Indenyl)CpTiCl$_2$ (3). This compound was prepared as for **2**. Yields were typically in the range of 40–50% of a red-brown powder which contained ca. 15% Cp_2TiCl_2. This impurity could be removed almost completely (ca. 3% remained) by washing with ether: ^1H NMR ($CDCl_3$) δ 6.21 (s, Cp), 7.68–7.36 (m, C_6 indenyl ring), 6.88 (t, J = 3.5 Hz), 6.67 (d, J = 3.5 Hz, C_5 indenyl ring).

Preparation of (1,2,4-Trimethylcyclopentadienyl)CpTiCl$_2$ (4). ⟨Cp⟩Li (2.28 g, 20 mmol) and $CpTiCl_3$ (4.38 g, 20 mmol) were allowed to react under the same conditions described for **2** (⟨Cp⟩Li is insoluble in THF, however), and worked up as for **2**. ⟨Cp⟩-$CpTiCl_2$ can be recrystallized from hot $CHCl_3$ or toluene to give scarlet plates; yield 2.72–3.25 g (48–56%). Typically, 5% or less of Cp_2TiCl_2 is observed in the crude reaction mixture under these conditions: ^1H NMR ($CDCl_3$) δ 6.43 (s, Cp), 6.26 (s, $C_5H_2Me_3$), 2.12 (s, $C_5H_2MeMe_2$), 2.07 (s, $C_5H_2MeMe_2$).

Preparation of (1,3-Diphenylcyclopentadienyl)CpTiCl$_2$ (5). A solution of (1,3-diphenylcyclopentadienyl)lithium (0.61 g, 2.7 mmol) in 10 mL of THF ((1,3-diphenylcyclopentadienyl)-lithium solutions appear to transmit red and fluoresce blue) was slowly added via cannula to a solution of $CpTiCl_3$ (592 mg, 2.7 mmol) in 10 mL of THF under Ar at room temperature. The purple-red solution was stirred for 30 min, and the solvent was removed in vacuo. The reaction mixture was extracted with a 1:1 benzene/dichloromethane mixture. Evaporation of the solvent yielded a dark purple-red microcrystalline powder. Extensive washing of this powder with EtOH and ether yielded 215 mg (20%) of **5**: ^1H NMR (CD_2Cl_2) δ 6.33 (s, Cp), 7.71–7.40 (m, $C_5H_3Ph_2$), 6.96 (d, J = 1 Hz, $C_5HH_2Ph_2$).

Preparation of [C$_5$(CH$_3$)$_5$]CpTiCl$_2$ (6). A suspension of CpLi (0.72 g, 10 mmol) in 10 mL of THF was added slowly via cannula to a stirred solution of Cp^*TiCl_3 (2.9 g, 10 mmol) in 10 mL of THF under an Ar atmosphere at ambient temperature. The reaction mixture was stirred for 30 min and worked up as for **2**. Examination of the crude reaction product indicated less than 5% $Cp^*_2TiCl_2$ was present (^1H NMR). Recrystallization of the red powder from hot toluene gave 1.47 g (46%) of pure **6** as deep red columnar crystals. A small amount was recrystallized from $CHCl_3$ for kinetics experiments: mp 184–185 °C dec (lit.[45] mp 185–186 °C); ^1H NMR ($CDCl_3$) δ 6.25 (s, Cp), 2.04 (s, C_5Me_5).

Preparation of Cp$_2$TiF$_2$. This is a procedure modified from the preparation of Cp_2ZrF_2.[38] Cp_2TiCl_2 (2.5 g, 10 mmol) and Li(O-*t*-Bu) (1.61 g, 20 mmol) were dissolved in 20 mL of THF and allowed to stir for 24 h under Ar at room temperature to give a yellow-orange solution. The solvent was removed in vacuo, and the resulting oil was extracted with petroleum ether. The petroleum ether extracts were filtered under Ar through a fine frit. The petroleum ether was removed in vacuo, leaving a yellow-orange liquid. ^1H NMR spectroscopy of this liquid dissolved in C_6D_6 showed it to be >90% $Cp_2Ti(O\text{-}t\text{-}Bu)_2$ (δ 5.98 (s, 10 H), 1.16 (s, 18 H)). The liquid was dissolved in 20 mL of ether, and $BF_3{\cdot}Et_2O$ (2.7 mL, 22 mmol) was slowly added by syringe. A pale orange powder precipitated rapidly. The powder was washed exhaustively with ether and dried in vacuo. The product proved to be too insoluble for NMR analysis in $CDCl_3$ and C_6D_6. Addition of one drop of D_2O to these suspensions in NMR tubes resulted in rapid dissolution of the orange suspension to give a yellow solution of Cp_2TiF_2 as verified by ^1H NMR spectroscopy. The rest of the orange powder [probably $Cp_2TiF(BF_4)$ or $Cp_2Ti(BF_4)_2$] was treated with 15 mL of MeOH followed by washing with ether. The yellow solid was dried in vacuo and sublimed at 120 °C at 10^{-6} torr onto a water-cooled probe; yield 1.2 g (56%) of fluffy, bright yellow powder. A small portion was recrystallized from hot toluene to yield fluffy yellow needles: ^1H NMR δ 6.41 (t, J_{FH} = 1.71 Hz). A small doublet (ca. 5% of total signal) appears at δ 6.49 (J = 1.71 Hz).

Preparation of $[C_5H_4CH_3]Cp\overline{TiCH_2AlMe_2Cl}$ (8). This compound was prepared by using the method of Tebbe[6,10] for **1**. $AlMe_3$ (9 mL of 2 M $AlMe_3$ in toluene, 18 mmol) was added via syringe to an Ar-flushed flask containing **7** (2.34 g, 8.9 mmol). The resulting deep red solution was stirred for 40 h at room temperature. The solvent and the byproduct $AlMe_2Cl$ were removed in vacuo to yield a deep red oil. The oil was dissolved in 10 mL of toluene, and more $AlMe_3$ was added (1 mL of 2 M toluene solution, 2 mmol). This solution was stirred for ca. 12 h. Removal of the solvent in vacuo resulted in an oil which slowly solidified to a waxy mass. This mass was extracted with 40–50 mL of *n*-hexane. The combined extracts were concentrated and cooled to −50 °C to obtain **8** as a powder. The powder was washed once with 2–3 mL of hexane and pumped dry under high vacuum; yield 530 mg (20%). This product contained ca. 5–10% **1** due to the presence of a small amont of Cp_2TiCl_2 in **7**.

Preparation of $[1,2,4\text{-}(CH_3)_3C_5H_2]Cp\overline{TiCH_2AlMe_2Cl}$ (10). $AlMe_3$ (4.6 mL of 2 M toluene solution, 9.2 mmol) was added via syringe into an Ar-flushed flask containing **4** (1.34 g, 4.6 mmol). The deep red solution was stirred for 28 h at room temperature. The volatiles were removed to yield a sticky solid which consisted of a 60:40 mixture of **10** and ⟨Cp⟩CpTiMeCl as determined by ^1H NMR spectroscopy. $AlMe_3$ (1.84 mmol) and 4 mL of toluene were added to the reaction flask, and the mixture was stirred for 24 h at 45 °C. Several such cycles were repeated until no ⟨Cp⟩CpTiMeCl was observed. After this extended reaction time, the resulting oil contained a significant amount of toluene-insoluble red solids.[15] The insoluble solids were filtered and the volatiles removed from the supernatant giving a deep red oil. The oil was triturated with hexane yielding a deep red mass of solids. The solids were extracted with hot hexane. The solvent was removed from the extracts yielding an oil which slowly crystallized to yield 890 mg of **10** which was ca. 85% pure by ^1H NMR spectroscopy. A 500-mg sample of this material was dissolved in 50 mL of hot hexane and filtered. The supernatant was concentrated to 15 mL and cooled to −50 °C to yield 110 mg of pure **10** as a pale red powder.

Reactions of Cp$_2$TiCl$_2$, Cp$_2$TiMeCl, Cp$_2$TiMe$_2$, and Cp$_2$TiF$_2$ with Alkylaluminums. Reactions were carried out in 5-mm NMR tubes capped with plastic caps or with latex septa (Wilmad Glass). All reactions were performed utilizing a total Ti concentration of 0.2 M in C_6D_6 solvent. Aluminum reagents were introduced via microsyringe. The compositions of reactions mixtures were measured by ^1H NMR spectroscopy and are considered accurate to within 5%.

Measurement of the Deuterium Isotope Effect. Cp_2TiCl_2 (25 mg, 0.1 mmol) was suspended in 500 μL of C_6D_6 in a NMR tube. A 10-μL sample of $AlMe_3$ (0.1 mmol) was added via syringe along with 142 μL of a 0.7 M toluene solution of $AlMe_3\text{-}d_9$ (0.1 mmol). ^1H and ^2H NMR spectra of the solution were recorded. The integrals of the species $Cp_2TiMeCl{\cdot}AlMe_{3-n}Cl_n$ were Cp (10.0), CH_3 (1.5), and AlMe (7.5). Integration of the ^2H spectrum gave a ratio of $TiCD_3$:$AlCD_3$ of approximately 3:13 (the signals overlapped somewhat). The sample was placed in a bath maintained at 56 °C. The progress of the reaction was monitored frequently by ^1H NMR spectroscopy. After 2 h there had been a 37% conversion to **1** (and **1**-d_n). The ratio of the integrals of the cyclopentadienyl resonances to the titanium methylene resonance was 10:1.49. The resonance at δ 8.28 was sharp and did not exhibit any apparent coupling to deuterium. After 44 h, the conversion to **1** and **1**-d_n was complete, and methyl benzoate (19 μL, 0.15 mmol) and pyridine (12 μL, 0.15 mmol) were added to the sample. ^1H NMR spectroscopy confirmed that the reaction had yielded 1-methoxy-1-phenylethylene: ^1H NMR O*Me*, δ 3.33; $=CH_AH_B$, δ 4.63 (d), 4.06 (d, J_{AB} = 2.8 Hz). The relative integrals of the methoxy group and the vinylic hydrogens was 1.49 ± 0.1:1. No Ph(OMe)C=CHD could be detected by examining the center of each vinylic doublet, even with resolution enhancement of the spectrum. The limit of detection is estimated to be ±10%.

Measurement of the Kinetics of the Reaction Cp$_2$TiCl$_2$ + Excess AlMe$_3$. A 5-mm NMR sample tube was loaded with Cp_2TiCl_2 (25.0 mg, 0.10 mmol) and taken into a drybox. The walls of the NMR tube were washed down with 400 μL of C_6D_6, and $AlMe_3$ (40 μL, 0.42 mmol) was added via syringe. The sample was capped, removed from the drybox, and agitated briefly to allow dissolution and formation of $Cp_2TiMeCl{\cdot}Al$. The sample was placed in the probe of the JEOL FX-90Q maintained at 53 °C, and spectra were obtained at regular intervals. An effective concentration of $AlMe_3$ at $t = 0$ was calculated from the relative integrals of the C_5H_5 and Ti–Me signals of $Cp_2TiMeCl{\cdot}Al$ and the total integral of the AlMe signal. Least squares analysis of second-order plots of ln *kt* vs. *t* yielded the rate constants. This procedure was repeated for several concentrations of the titanium and aluminum reagents and at several different temperatures. Activation parameters were obtained from least squares analysis of ln k/T vs. $1/T$ plots.

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Registry No. **1**, 67719-69-1; **2**, 79269-70-8; **3**, 33071-07-7; **4**, 87738-99-6; **5**, 87729-04-2; **6**, 38496-87-6; **7**, 1282-43-5; **8**, 87729-05-3; **9**, 87739-00-2; **10**, 87739-01-3; **11**, 87729-06-4; **12**, 87729-07-5; $CpTiCl_3$, 1270-98-0; $TiCl_4$, 7550-45-0; Cp_2TiCl_2, 1271-19-8; $[C_5H_4(CH_3)]_2TiCl_2$, 1282-40-2; $Cp^{tms}Li$, 76514-39-1; ⟨Cp⟩Li, 87729-03-1; CpLi, 16733-97-4; Cp^*TiCl_3, 12129-06-5; $Cp_2Ti(O\text{-}t\text{-}Bu)_2$, 87729-08-6; $Cp_2TiMeCl$, 1278-83-7; Cp_2TiMe_2, 1271-66-5; Cp_2TiF_2, 309-89-7; methylcyclopentadienyllithium, 54061-45-9; (1,3-diphenylcyclopentadienyl)lithium, 58813-26-6; ^1H-indenyllithium, 32334-19-3; trimethylaluminum, 75-24-1.

Highly Reduced Organometallics. 16.[1] Synthesis, Isolation, and Characterization of the Tricarbonylcyclopentadienylmetalate(2–) Anions of Niobium and Tantalum, $C_5H_5M(CO)_3{}^{2-}$

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Treatment of $C_5H_5M(CO)_4$ (M = Nb, Ta) with sodium in liquid ammonia at –78 °C generates the corresponding disodium salts $Na_2[C_5H_5M(CO)_3]$, which have been spectroscopically identified. Cesium iodide reacts with $Na_2[C_5H_5M(CO)_3]$ in liquid ammonia to provide 70–80% isolated yields of pale orange, air-sensitive solids that analyze satisfactorily as the unsolvated dicesium salts $Cs_2[C_5H_5M(CO)_3]$. These are the first isolated salts containing the tricarbonylcyclopentadienylmetalate dianions of niobium and tantalum. Reactions of $C_5H_5M(CO)_3{}^{2-}$ with CH_3CN, Et_4N^+, or other weak Brønsted acids or Ph_3SnCl provide, after cation exchange, 40–70% isolated yields of $[Et_4N][C_5H_5M(CO)_3H]$ or $[Et_4N][C_5H_5M(CO)_3SnPh_3]$, which are characterized by elemental analyses and IR and ^1H NMR spectra.

Introduction

For over 20 years, the only example of a cyclopentadienyl-substituted metal carbonyl dianion was $C_5H_5V(CO)_3{}^{2-}$,[2] originally prepared by Fischer and Vigoureux,[3] by the method shown in eq 1. Very recently,

$$C_5H_5V(CO)_4 + 2Na \xrightarrow{NH_3} Na_2[C_5H_5V(CO)_3] + CO \qquad (1)$$

$Na_2[C_5H_5Nb(CO)_3]$ has also been identified by IR spectroscopy as a product formed during the reduction of $C_5H_5Nb(CO)_4$ by Na–Hg in THF.[5] In this paper, we report the characterization and first isolation of salts containing $C_5H_5M(CO)_3{}^{2-}$ (M = Nb, Ta) as well as triphenylstannyl and hydride derivatives of these highly reactive materials. These dianions are likely to be important precursors to a variety of new organoniobium and organotantalum complexes, including mixed-metal clusters containing these elements.

Experimental Section

General Procedures and Materials. All operations were performed under an atmosphere of nitrogen further purified by passage through columns of activated BASF catalyst, anhydrous magnesium perchlorate, and molecular sieves. Solutions were transferred via stainless steel cannulas and syringes; otherwise reactions were generally performed by using standard Schlenk apparatus with a double manifold vacuum line. Ammonia was dried with Na metal and distilled in vacuo directly into the reaction vessel. Reagent grade acetonitrile was dried with CaH_2, freed of oxygen by a nitrogen purge, and distilled immediately before use. Reagent grade tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were distilled from alkali-metal benzophenone ketyls before use. Reagent grade acetone, heptane, absolute ethanol, and isopentane were freed of oxygen by purging with nitrogen for 1–2 h before use. Published procedures for the synthesis of $C_5H_5M(CO)_4$ (M = Nb, Ta),[6] $[Na(diglyme)_2][M(CO)_6]$,[7] and $[Na(DME)]C_5H_5$[8] were employed. All other reactants and solvents were obtained from commercial sources and used without further purification.

Dicesium Tricarbonylcyclopentadienyltantalate(2–), $Cs_2[C_5H_5Ta(CO)_3]$ (1). Liquid ammonia (100 mL) was distilled into a flask containing a glass stir bar, $C_5H_5Ta(CO)_4$ (0.50 g, 1.40 mmol), and sodium metal (0.10 g, 4.2 mmol) at –70 °C. Within 1.5 h after the reaction mixture had warmed to –33 °C, the initial blue solution had changed to an orange color. This solution of $Na_2[C_5H_5Ta(CO)_3]$ was filtered at –70 °C into a flask containing a glass stir bar and a solution of CsI (1.45 g, 5.58 mmol) in 10 mL of liquid ammonia. After about 2–3 min a finely divided orange solid precipitated. The orange slurry was filtered at –70 °C, washed with liquid ammonia (1 × 75 mL, 1 × 50 mL), and dried

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[1] Part 15: Lin, J. T.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 6252.

[2] Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1.

[3] Fischer, E. O.; Vigoureux, S. *Chem. Ber.* **1958**, *91*, 2205.

[4] Hoyano, J. K.; Graham, W. A. G. *Organometallics* **1982**, *1*, 783.

[5] Näumann, F.; Rehder, D.; Pank, V. *J. Organomet. Chem.* **1982**, *240*, 363.

[6] Werner, R. P. M.; Filbey, A. H.; Manastyrskyj, S. A. *Inorg. Chem.* **1964**, *3*, 298.

[7] Dewey, C. G.; Ellis, J. E.; Fjare, K. L.; Pfahl, K. M.; Warnock, G. F. P. *Organometallics* **1983**, *2*, 388.

[8] Smart, J. C.; Curtis, C. J. *Inorg. Chem.* **1977**, *16*, 1788.

0276-7333/84/2303-0230$01.50/0