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 (45) "Cu(cyclops)<sup>+</sup>" refers in this context to the species which results when [Cu(cyclops)]ClO<sub>4</sub>·H<sub>2</sub>O is dissolved in the given solvent system. Axial ligation should occur with solvent in the axial position.  
 (46) Preliminary data analysis gives an approximate value of *K*<sub>1</sub>, which enables [L] to be computed from the known [Cu] and total added L concentration. The correction is, of course, quite small when [L] ≫ [Cu].  
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## New Reagents for the Synthesis of Paramagnetic Organometallic, Amide, and Coordination Complexes of Trivalent Titanium, Vanadium, and Chromium

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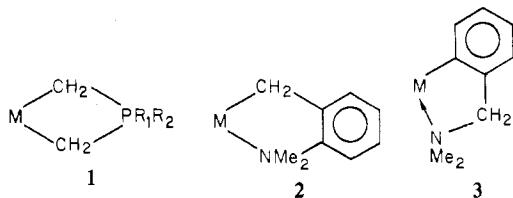
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The tetrahydrofuran complexes, MCl<sub>3</sub>(THF)<sub>3</sub> (M = Ti, V, Cr), react with 1 equiv of a 1,3-diketone (diket) in THF to give the air-sensitive, paramagnetic complexes M(diket)Cl<sub>2</sub>(THF)<sub>2</sub>. Reactions of these reagents with LiC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>, LiCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>, and LiN(SiMe<sub>3</sub>)<sub>2</sub> give novel, air-sensitive organometallic and amide complexes. The coordinated THF may be readily displaced by neutral ligands such as PMe<sub>3</sub> and bipyridine to give new coordination compounds. Magnetic and spectroscopic data are presented with detailed synthetic procedures.

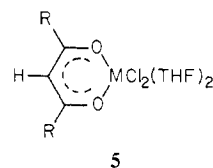
### Introduction

We are currently investigating the coordination and organometallic chemistry of the early transition metals, with particular emphasis on paramagnetic compounds. Generally, paramagnetic organometallic complexes are less stable than their diamagnetic analogues. For example, while Cp<sub>2</sub>MH<sub>2</sub> (where M = Mo and W and Cp = cyclopentadienide) are well-known, thermally stable compounds<sup>1</sup> Cp<sub>2</sub>TaH<sub>2</sub> and Cp<sub>2</sub>NbH<sub>2</sub><sup>2</sup> are very reactive and unstable below room temperature.

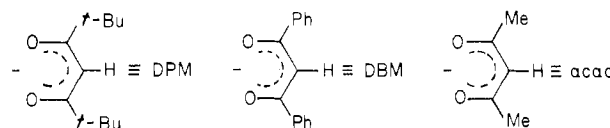
Chelated organic ligands, such as 1-3, have been found<sup>3-6</sup>



to greatly enhance the thermal stability of paramagnetic organometallic compounds, and some interesting chemistry has evolved. The reactions of organolithium reagents with CrCl<sub>2</sub> give compounds of the type [Li<sub>2</sub>(sol)CrR<sub>2</sub>]<sub>2</sub><sup>7,8</sup> (where sol = coordinating solvent such as dioxane or tetrahydrofuran), 4. These compounds were *diamagnetic* and dimeric with quadruple metal-metal bonds postulated to account for the diamagnetism. In contrast, the lithium salts of 2 and 3 reacted with CrCl<sub>2</sub> to give *paramagnetic* organometallic compounds.<sup>9</sup> The interesting chemistry and unusual stability of these paramagnetic organometallic compounds prompted us to search for new systems containing chelating ligands. Our objectives were twofold: (1) to find a chelating ligand capable of stabilizing electron-rich paramagnetic organometallics by delocalization of electron density and (2) to find new reagents for the synthesis of early transition metal organometallic and coordination compounds. The diketone ligand satisfied both requirements.<sup>5</sup> In this paper are described detailed preparations and some chemistry of the series of compounds 5, where M = Ti, V, or Cr, R = Me, Ph, or *t*-Bu, and THF = tetrahydrofuran.



rahydrofuran. The following abbreviations will be used for the diketone ligands throughout the paper:

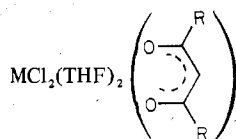


### Results

**A. M(diket)Cl<sub>2</sub>(THF)<sub>2</sub> Complexes.** The addition of a molar equivalent of a 1,3-diketone to a suspension of CrCl<sub>3</sub>(THF)<sub>3</sub> or TiCl<sub>3</sub>(THF)<sub>3</sub> in dry THF under an inert atmosphere gave an immediate reaction, liberating HCl. From these solutions crystalline, air-sensitive solids, whose analytical data were consistent with the formulation M(diket)Cl<sub>2</sub>(THF)<sub>2</sub>, were isolated nearly quantitatively. The DPM compounds are soluble in benzene, ether, THF, and toluene, whereas the acac and DBM compounds are much less soluble in these solvents. All of the compounds are quite soluble and stable in dry, oxygen-free dichloromethane, so it is an excellent solvent for recrystallizations and solution spectral and magnetic moment measurements.

The vanadium complexes 5 were isolated in only low yields from reactions of the 1,3-diketones with VCl<sub>3</sub>(THF)<sub>3</sub> in THF. Improved yields were obtained by preforming the diketone anion and reacting this salt with VCl<sub>3</sub>(THF)<sub>3</sub>. Thus, DBM<sup>-</sup> was dissolved in THF and solid KH was slowly added. When the formation of K<sup>+</sup>DBM<sup>-</sup> was complete, as indicated by the absence of hydrogen gas evolution, the THF solution of this salt was added to a solution of VCl<sub>3</sub>(THF)<sub>3</sub>. KCl precipitated rapidly and VCl<sub>2</sub>(THF)<sub>2</sub>(DBM) was isolated in excellent yield. Large quantities of these reagents can easily be prepared directly from the appropriate anhydrous metal halide by

Table I. Electronic, Electron Spin Resonance and Magnetic Moment Data for Complexes of the Type



M	R	Solvent	Electronic spectrum		Electron spin resonance data				Magnetic moments							
			Wavelength, nm	Molar extinction coeff <sup>a</sup>	Solvent	Temp, °C	<i>g</i>	$\langle a_M \rangle$ , G	Solvent	$\mu_{\text{eff}}$ , $\mu_B$						
Ti	<i>t</i> -Bu	Toluene	399	563	PhMe	35	1.954	15.2	CH <sub>2</sub> Cl <sub>2</sub>	1.95						
			471	556												
			550	661												
	Ph	THF	466	4312	PhMe	35	1.950	13.0	CH <sub>2</sub> Cl <sub>2</sub>	1.76						
			492	4450												
			635	5504												
			705	8073												
			755	8027												
			392	375							THF	-60	1.942	15.2	CH <sub>2</sub> Cl <sub>2</sub>	1.88
460	692															
540	660															
V	<i>t</i> -Bu	THF	466	160 sh	THF	35	1.965	111.4	C <sub>6</sub> H <sub>6</sub>	2.68						
			582	39												
	Ph	THF	523	307 sh	THF	35	1.965	111.4	CH <sub>2</sub> Cl <sub>2</sub>	2.69						
Me	THF	686	20													
Cr	<i>t</i> -Bu	THF	387 sh		THF	35	1.965	111.4	CH <sub>2</sub> Cl <sub>2</sub>	3.80						
			405	73												
			425 sh													
			465	45												
			630	15												
			715 sh													
			641	44							THF	35	1.965	111.4	CH <sub>2</sub> Cl <sub>2</sub>	3.71
			713	31												
			390 sh													
			400	143							THF	35	1.965	111.4	CH <sub>2</sub> Cl <sub>2</sub>	3.71
			418 sh													
			464	63												
	638	39	THF	35	1.965	111.4	CH <sub>2</sub> Cl <sub>2</sub>	3.71								
	715 sh															

<sup>a</sup> Units of L mol<sup>-1</sup> cm<sup>-1</sup>.

forming the tris(tetrahydrofuran) compounds in situ. VCl<sub>3</sub>(THF)<sub>3</sub> and TiCl<sub>3</sub>(THF)<sub>3</sub> are formed quantitatively in less than 2 h from VCl<sub>3</sub> and TiCl<sub>3</sub> in refluxing THF. In order to prepare CrCl<sub>3</sub>(THF)<sub>3</sub>, in situ, from CrCl<sub>3</sub>, approximately 0.1% zinc powder is added to catalyze the reaction. The small amount of zinc chloride that is formed can be separated from Cr(diket)Cl<sub>2</sub>(THF)<sub>2</sub> by recrystallization.

The electronic spectra of the complexes were measured in solution in the visible region from 375 to 800 nm. The positions of the absorption bands and their molar extinction coefficients are given in Table I.

The electronic spectrum of Cr(DPM)Cl<sub>2</sub>(THF)<sub>2</sub>, which is very similar to the spectrum of Cr(acac)Cl<sub>2</sub>(THF)<sub>2</sub>, is shown in Figure 1. Each spectrum exhibits three broad bands with shoulders on either side. Ti(DPM)Cl<sub>2</sub>(THF)<sub>2</sub> and Ti(acac)Cl<sub>2</sub>(THF)<sub>2</sub> also have very similar electronic spectra with three intense absorption bands in the visible region. The chromium and titanium complexes containing DBM bear no resemblance to the acac and DPM complexes. A possible explanation is that DPM and acac both contain alkyl substituents on the ketonic carbons while DBM has a phenyl substituent.

The vanadium complexes showed only weak absorptions in the visible region and there does not appear to be any similarity in the spectra of the three complexes.

The electron spin resonance spectra in toluene at 35 °C of the titanium complexes (Table I) showed very sharp resonances flanked by <sup>47,49</sup>Ti satellites. The ESR spectra of V(DPM)Cl<sub>2</sub>(THF)<sub>2</sub> and V(acac)Cl<sub>2</sub>(THF)<sub>2</sub> at 35 °C exhibited eight lines at *g* = 1.965 due to coupling of the electron with the <sup>51</sup>V

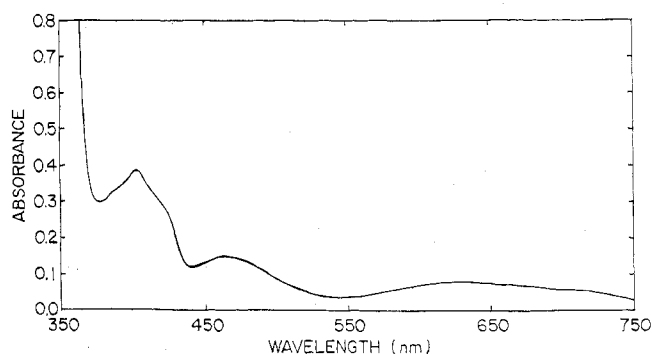
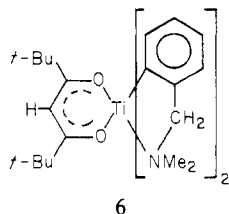


Figure 1. Electronic spectrum of CrCl<sub>2</sub>(DPM)(THF)<sub>2</sub> in THF (6.77 × 10<sup>-3</sup> M).

(*I* = 7/9, 99.8% natural abundance) nucleus. The chromium complexes and V(DBM)Cl<sub>2</sub>(THF)<sub>2</sub> gave no ESR spectra in solution to -60 °C and gave only broadened, unresolved, NMR spectra.

The magnetic moments (Table I) were determined in dichloromethane by the Evans technique<sup>10</sup> and ranged from 1.8 to 1.9, 2.6 to 2.7, and 3.7 to 3.9  $\mu_B$  for the titanium, vanadium, and chromium complexes, respectively. These values are in the range expected for octahedral d<sup>1</sup>, d<sup>2</sup>, and d<sup>3</sup> electronic configurations of trivalent Ti, V, and Cr.<sup>11</sup>

**B. Organometallic Derivatives.** The addition of 2 molar equiv of LiC<sub>6</sub>H<sub>4</sub>-*o*-CH<sub>2</sub>NMe<sub>2</sub> to a solution of Ti(DPM)Cl<sub>2</sub>(THF)<sub>2</sub> in ether, at room temperature under an inert atmosphere, gave an immediate dark green solution from which LiCl rapidly precipitated. From this solution, **6** was

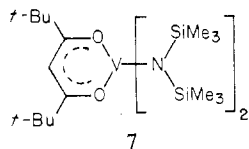


isolated in ~70% yield as a dark green, very air-sensitive crystalline solid. It decomposes over a period of several days when stored under a nitrogen atmosphere at room temperature but may be stored for months at  $-40^{\circ}\text{C}$  without any apparent decomposition. Its electronic spectrum is typical of octahedral  $d^1$  complexes<sup>12</sup> with absorption bands at 385 and 656 nm. The magnetic moment of  $1.7 \mu_B$  is also consistent with trivalent titanium. Hydrolysis of a benzene solution of **2** with  $\text{D}_2\text{O}$  gave  $\text{C}_6\text{H}_4\text{DCH}_2\text{NMe}_2$ , confirming the metalation of the benzyl-dimethylamino ligand.

The vanadium analogue of **6** was isolated from the reaction of  $\text{LiC}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2$  with  $\text{V(DPM)Cl}_2(\text{THF})_2$  in ether as a dark maroon, air-sensitive crystalline solid. The magnetic moment ( $2.75 \mu_B$ ) implies the presence of two unpaired electrons. The electronic spectrum shows four absorption bands between 450 and 592 nm with extinction coefficients of 700–1100, so they are probably charge transfer in origin. Unlike the titanium analogue, it may be stored for months under an inert atmosphere at room temperature with little or no decomposition.

The chelated benzyl lithium reagent,  $\text{LiCH}_2\text{-}o\text{-C}_6\text{H}_4\text{NMe}_2$ ,<sup>6</sup> **2**, reacted cleanly with  $\text{Cr(DPM)Cl}_2(\text{THF})_2$  and  $\text{Ti(DPM)Cl}_2(\text{THF})_2$  to give  $(\text{DPM})\text{M}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2)_2$  as red-brown and dark green crystalline solids.  $\text{Ti(DPM)(CH}_2\text{C}_6\text{H}_4\text{NMe}_2)_2$  is much more reactive than **6** and decomposes overnight at room temperature and slowly at  $-30^{\circ}\text{C}$ . The magnetic moment and electronic spectra (Table II) are consistent with octahedral trivalent metal ions. The mass spectrum of  $\text{Cr(DPM)(CH}_2\text{C}_6\text{H}_4\text{NMe}_2)_2$  at  $150^{\circ}\text{C}$  showed a parent ion peak at  $m/e$  503.2697 (calculated 503.2730). Strong peaks were observed at  $m/e$  369, 268, 235, and 134.

**C. Disilylamido Complexes.** Two equivalents of  $\text{LiN}(\text{SiMe}_3)_2$  was added to a well-stirred solution of  $\text{V(DPM)Cl}_2(\text{THF})_2$  in pentane to give a dark solution from which  $\text{LiCl}$  rapidly precipitated. From the solution, **7** was isolated as a



red-purple crystalline solid in 89% yield. It is very soluble in hydrocarbon solvents and may be sublimed at  $125^{\circ}\text{C}$  and  $10^{-4}$  mmHg. Similarly,  $\text{V(DBM)[N}(\text{SiMe}_3)_2]_2$ ,  $\text{Ti(DPM)[N}(\text{SiMe}_3)_2]_2$ , and  $\text{Ti(DBM)[N}(\text{SiMe}_3)_2]_3$  were isolated as intensely colored crystalline solids. The magnetic moment data and electronic spectral data are listed in Table II. The electronic spectra in the visible region showed several bands with large molar extinction coefficients which would suggest that the bands are due to charge transfer.

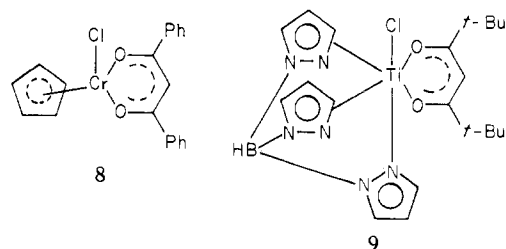
The mass spectra of the four silylamido complexes showed nothing higher than the parent ion peak.

**D. Some Coordination Compounds.** The chloride and coordinated THF ligands are quite labile and are readily displaced by a variety of ligands. A few of these reactions have been examined and are briefly described.

The addition of 2 equiv of trimethylphosphine to an ether solution of  $\text{Ti(DPM)Cl}_2(\text{THF})_2$  under nitrogen gave a deep blue solution from which  $\text{Ti(DPM)Cl}_2(\text{PMe}_3)_2$  was precipitated, by the addition of hexane, as a dark blue crystalline,

air-sensitive solid. The ESR spectrum in toluene at  $-60^{\circ}\text{C}$  gave a triplet at  $g = 1.958$  flanked by  $^{47,49}\text{Ti}$  satellites ( $\langle a_{\text{Ti}} \rangle = 12.2 \text{ G}$ ). The triplet arises from hyperfine coupling of the electron with two equivalent  $^{31}\text{P}$  nuclei. Similarly,  $\text{Cr(DPM)Cl}_2(\text{PMe}_3)_2$  was isolated from the reaction of  $\text{PMe}_3$  with  $\text{Cr(DPM)Cl}_2(\text{THF})_2$  as a dark red, crystalline solid. The chelating ligand, 2,2'-bipyridyl (bpy), displaces THF to give  $\text{Ti(DPM)Cl}_2(\text{bpy})$ . The electronic spectra and magnetic moment data for the bipyridyl and  $\text{PMe}_3$  complexes are consistent with octahedral  $d^1$  and  $d^3$  complexes.

Thallium cyclopentadienide and potassium hydrotris(1-pyrazolyl)borate ( $\text{KHBpz}_3$ ) reacted cleanly with  $\text{Cr(DBM)Cl}_2(\text{THF})_2$  and  $\text{Ti(DPM)Cl}_2(\text{THF})_2$  to give **8** and **9**,

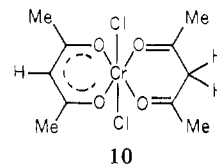


respectively. The compositions were confirmed by elemental and spectral analyses.

### Discussion

There are relatively few good reagents for investigating the organometallic and coordination chemistry of the early transition metals. The most widely used compounds for the synthesis of  $\text{Cr(III)}$ ,  $\text{Ti(III)}$ , and  $\text{V(III)}$  compounds are the tris(tetrahydrofuran) compounds  $\text{MCl}_3(\text{THF})_3$ . Generally, these reagents are more versatile than the polymeric, insoluble, anhydrous metal halides but occasionally problems arise. For example, the three-coordinate amide<sup>13</sup> and alkyl complexes<sup>14</sup>  $\text{M}[\text{CH}(\text{SiMe}_3)_2]_3$ ,  $\text{M}[\text{CH}_2\text{SiMe}_3]_3$ , and  $\text{M}[\text{N}(\text{SiMe}_3)_2]_3$  could not be prepared from  $\text{MCl}_3(\text{THF})_3$  (where  $\text{M} = \text{Ti}$  or  $\text{V}$ ). A successful synthesis was performed using  $\text{MCl}_3(\text{NMe}_3)_2$ . In search of alternate sources of soluble reactive reagents of  $\text{Cr(III)}$ ,  $\text{Ti(III)}$ , and  $\text{V(III)}$  we have discovered a new class of compounds,  $\text{M(diket)Cl}_2(\text{THF})_2$ . The use of the diketonate ligand offers a distinct advantage over other reagents in that large variations in solubility and steric and electronic effects about the metal can easily be made by simply changing the 1,3-diketone ligand.

Several years ago Kawaguchi et al.<sup>15</sup> prepared a number of molecular acetylacetonate complexes of first-row transition metals. When they dissolved  $\text{CrCl}_3(\text{THF})_3$  in acetylacetonate, a dark green complex, **10**, was isolated. The compound was



presumably formed by displacement of THF from  $\text{Cr}(\text{acac})\text{Cl}_2(\text{THF})_2$  which must be formed as an intermediate. The structure postulated for **10** was based on a far-infrared spectroscopic study. The electronic spectra of  $\text{Cr(DPM)Cl}_2(\text{THF})_2$  and  $\text{Cr}(\text{acac})\text{Cl}_2(\text{THF})_2$  are nearly identical with the spectrum reported for **10**. Therefore, it is likely that similar stereochemistries exist for **5** with trans chloride atoms and THF coordinated in the two positions trans to the diketonate ligand. Further evidence for the geometry stems from the fact that equivalent phosphine ligands are present in  $\text{Ti(DPM)Cl}_2(\text{PMe}_3)_2$  (vide supra) and its electronic spectrum is similar to that of  $\text{Ti(DPM)Cl}_2(\text{bpy})$ . Since the latter compound contains a bidentate ligand it must coordinate in two adjacent sites (ignoring bridging, which is unlikely for bpy).

Table II. Electronic and Magnetic Moment Data for Some Organometallic, Amide, and Coordination Compounds of Ti(III), V(III), and Cr(III)

Compound <sup>a</sup>	Solvent	Electronic spectra		Magnetic moments	
		Wavelength, nm	Extinction coefficient <sup>b</sup>	Solvent	$\mu_{\text{eff}}$ , $\mu_B$
Ti(DPM)(C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	390 656	450 997	C <sub>6</sub> H <sub>6</sub>	1.75
Ti(DPM)(CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	620	328	CH <sub>2</sub> Cl <sub>2</sub>	3.88
Cr(DPM)(CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	546 681	130 21		
V(DPM)(C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	450 505 547 592	950 1085 1032 778		
Cr(DBM)( $\pi$ -Cp)Cl	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	535 610	199 271	CH <sub>2</sub> Cl <sub>2</sub>	3.64
Ti(DPM)(HBpz <sub>3</sub> )Cl	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	400 468	400 264	CH <sub>2</sub> Cl <sub>2</sub>	2.01
Ti(DPM)(PMe <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	400 568 sh 605 658 sh	647 851 931 851	CH <sub>2</sub> Cl <sub>2</sub>	1.82
Cr(DPM)(PMe <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	410 450 590	167 149 142	CH <sub>2</sub> Cl <sub>2</sub>	3.99
Ti(DPM)(bpy)Cl <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	400 485 583 647 sh	468 408 707 598	CH <sub>2</sub> Cl <sub>2</sub>	1.72
Ti(DPM)[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	387 400 530 sh 579 sh 649 780	1496 1551 1246 2355 4571 2687	CH <sub>2</sub> Cl <sub>2</sub>	1.91
Ti(DBM)[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	593 650 880	230 270 641	CH <sub>2</sub> Cl <sub>2</sub>	2.06
V(DPM)[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	380 394 451 515 637	1139 1122 1016 1260 680	CH <sub>2</sub> Cl <sub>2</sub>	2.98
V(DBM)[N(SiMe <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	456 479 629 753	1559 1426 1973 1559	CH <sub>2</sub> Cl <sub>2</sub>	3.07

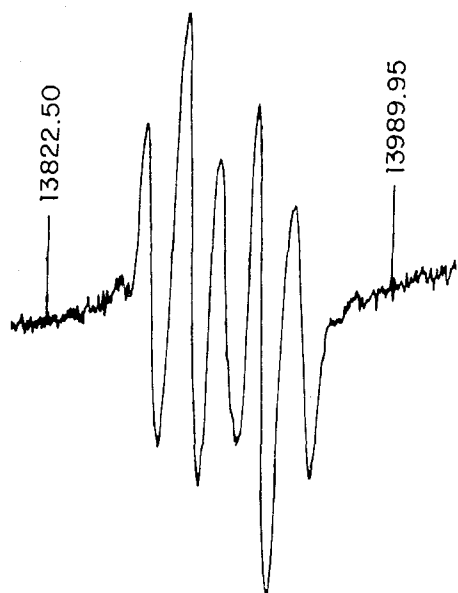
<sup>a</sup> DPM = anion of dipivalolymethane; DBM = anion of dibenzoylmethane. <sup>b</sup> Units in L mol<sup>-1</sup> cm<sup>-1</sup>.

As noted by Kawaguchi et al.,<sup>15</sup> the addition of a large excess of acetylacetonone does not result in further elimination of HCl from Cr(acac)Cl<sub>2</sub>(acacH). We have examined the titanium system in more detail and find that the addition of a second equivalent of DPMH to a solution of Ti(DPM)Cl<sub>2</sub>(THF)<sub>2</sub> in benzene has no effect. However, the addition of 1 equiv of NEt<sub>3</sub> caused an immediate reaction, and triethylammonium chloride precipitated. From this solution was isolated Ti(DPM)<sub>2</sub>Cl in 89% yield as a very soluble, deep blue compound. A similar attempt to isolate Cr(DPM)<sub>2</sub>Cl gave only Cr(DPM)<sub>3</sub>.

Bradley and co-workers<sup>13</sup> have prepared a number of very interesting compounds of the first-row transition metals using the bulky hexamethyldisilylamide ligand N(SiMe<sub>3</sub>)<sub>2</sub>. Because of large ligand size, compounds of low coordination numbers are obtained. The unusual three-coordinate trigonal complexes, M[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>, of trivalent titanium, vanadium, and chromium, were obtained. The reaction of M(diket)Cl<sub>2</sub>(THF)<sub>2</sub> (M = Ti or V, diket = DPM or DBM) with 2 equiv of LiN(SiMe<sub>3</sub>)<sub>2</sub> has given intensely colored crystalline solids, (diket)M[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>. Their infrared spectra do not show absorption bands near 1700 cm<sup>-1</sup> attributable to a ketonic-type vibration. Therefore, the diketone ligand is probably bidentate and the compounds are rare examples of four-coordinate Ti(III) and V(III).

The lithium reagents of **2** and **3** react with M(diket)Cl<sub>2</sub>(THF)<sub>2</sub> to give six-coordinate octahedral, paramagnetic organometallic complexes. A number of six-coordinate organochromium(III) compounds are known;<sup>7,8</sup> however, there are few examples of well-characterized octahedral V(III) and Ti(III) compounds although they are often postulated as intermediates in Ziegler-Natta olefin polymerizations. The ESR spectrum of (DPM)Ti(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>)<sub>2</sub>, shown in Figure 2, consists of a doublet of triplets centered at  $g = 2.001$  and hydrogen hyperfine coupling constants of 4.3 and 7.6 G. The low value is similar to that found in [Cp<sub>2</sub>TiMe<sub>2</sub>]<sup>-16</sup> and is consistent with a Ti-C-H interaction. The ESR data rule out the possibility of equivalent -CH<sub>2</sub>- groups and indicate that the electron couples to both hydrogens on one benzylic carbon and to only one hydrogen on the second CH<sub>2</sub> group. The reason for nonequivalent hydrogen atoms on one methylene carbon is not obvious; however, it is not unprecedented. The ESR spectrum of Cp<sub>2</sub>Ti(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>)<sub>2</sub><sup>6</sup> shows a doublet, flanked by titanium satellites ( $\langle a_{Ti} \rangle = 7.2$  G), centered at  $g = 1.981$ , which arises from coupling of the electron with only one hydrogen atom ( $\langle a_H \rangle = 5.1$  G).

The reaction of Ti(DPM)Cl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> with LiMe in ether gave a dark green solution from which fluffy green crystals were isolated. The compound is extremely air sensitive and good analytical data were hard to obtain. Although the



**Figure 2.** Electron spin resonance spectrum of  $\text{Ti}(\text{DPM})\text{-(CH}_2\text{C}_6\text{H}_4\text{NMe}_2)_2$ . Proton NMR field markers are in kilohertz.

analysis is close to  $\text{Ti}(\text{DPM})\text{Me}_2(\text{PMe}_3)_2$ , the exact structure is uncertain.

The improved stability of the organometallic complexes containing the diketone ligand as well as formation of four-coordinate amide complexes illustrates that the new compounds  $\text{M}(\text{diket})\text{Cl}_2(\text{THF})_2$  may be very versatile synthetic reagents.

### Experimental Section

All reactions were performed in a Vacuum Atmospheres drybox under an atmosphere of dry nitrogen. The solvents were dried by passage through columns of molecular sieves (Linde Grade 4A) and sparged with nitrogen prior to use.

Anhydrous metal halides were obtained from Research Organic/Research Inorganic, Inc. All other reagents were obtained commercially and were used without further purification.

Elemental analyses were performed by the Physical and Analytical Division of this department and by Alfred Bernhardt (Wert, West Germany).

**Preparation of  $\text{TiCl}_2(\text{THF})_2(\text{DPM})$ .** A suspension of  $\text{TiCl}_3$  (35.0 g, 0.227 mol) was refluxed in 500 mL of THF for 2 h and then cooled and DPMH (41.8 g, 0.227 mol) was added dropwise. When the addition was completed, the solution was stirred for 1 h, filtered, and stripped to dryness to give dark red-purple crystals that were washed from the flask with pentane and collected. Yield 97.0 g (96%), mp  $>300^\circ\text{C}$ .

Anal. Calcd for  $\text{TiCl}_2\text{O}_4\text{C}_{19}\text{H}_{35}$ : C, 51.13; H, 7.90; Cl, 15.89; Ti, 10.73. Found: C, 50.93; H, 7.47; Cl, 15.45; Ti, 10.43.

**Preparation of  $\text{TiCl}_2(\text{THF})_2(\text{DBM})$ .**  $\text{TiCl}_3$  (13.7 g, 89.1 mmol) was refluxed with stirring in 200 mL of THF for 90 min. The solution was cooled and DBMH (20.0 g, 89.1 mmol) was added dropwise with stirring. The solution became deep green and after stirring for 1 h it was filtered to give a crop of dark green crystals. The solvent volume was reduced to about 100 mL by rotary evaporation and about 100 mL of ether was added. The solution was filtered and the crystals were washed with pentane. Yield 43 g (100%), mp 160–165  $^\circ\text{C}$ .

Anal. Calcd for  $\text{TiCl}_2\text{O}_4\text{C}_{23}\text{H}_{27}$ : C, 56.81; H, 5.60; O, 13.16; Ti, 9.85. Found: C, 56.44; H, 5.79; O, 12.75; Ti, 8.78.

**Preparation of  $\text{TiCl}_2(\text{THF})_2(\text{acac})$ .** To a stirred solution of  $\text{TiCl}_3(\text{THF})_3$  (10.0 g, 26.7 mmol) in benzene was added acacH (2.70 g, 26.7 mmol). The solution rapidly turned red and deposited a red-purple crystalline precipitate. After stirring overnight the solution was filtered and washed with pentane. Yield 8.73 g (90%), mp 169–170  $^\circ\text{C}$ .

Anal. Calcd for  $\text{TiCl}_2\text{O}_4\text{C}_{13}\text{H}_{23}$ : C, 43.11; H, 6.40; Cl, 19.58. Found: C, 42.35, 42.36, 42.42; H, 6.07, 6.06, 6.03; Cl, 20.47.

**Preparation of  $\text{TiCl}(\text{DPM})_2$ .** To a suspension of  $\text{TiCl}_3$  (5.0 g, 32.4 mmol) in 200 mL of benzene was added triethylamine (8.0 g, 79 mmol). The solution was stirred and DPMH (12.1 g, 64.8 mmol)

was added. The solution rapidly turned deep blue and triethylammonium chloride precipitated. After stirring overnight, the solution was evaporated to dryness. Pentane was added and the solution was filtered. The ammonium salt was washed with pentane until the washings were colorless and the pentane was evaporated to give dark blue-purple crystals. Yield was 13.0 g (89%), mp 82  $^\circ\text{C}$ .

Anal. Calcd for  $\text{C}_{22}\text{H}_{38}\text{ClO}_4\text{Ti}$ : C, 58.73; H, 8.51; Ti, 10.65; Cl, 7.88. Found: C, 56.19; H, 8.41; Ti, 10.82; Cl, 7.96.

**Preparation of  $\text{VCl}_2(\text{THF})(\text{DPM})$ .** DPMH (3.45 g, 18.7 mmol) was added, dropwise, to a stirred solution of  $\text{VCl}_3(\text{THF})_3$  (7.0 g, 18.7 mmol) in benzene. The color rapidly turned yellow-brown and after stirring for 2 h the solution was filtered and the solvent removed to give a yellow-brown oil. Ether was added and the solution was filtered to give 2.43 g of a solid which was identified as  $\text{VCl}_3(\text{THF})_3$ . The filtrate was reduced in volume and pentane was added to give dark green crystals that were filtered off and washed with pentane. Yield 1.60 g (23%), mp 84–86  $^\circ\text{C}$ .

Anal. Calcd for  $\text{VCl}_2\text{O}_3\text{C}_{15}\text{H}_{27}$ : C, 47.75; H, 7.21; O, 12.73; Cl, 18.80. Found: C, 48.24, 48.18; H, 7.02, 7.15; Cl, 20.62; O, 12.25, 12.57, 12.15.

**Preparation of  $\text{VCl}_2(\text{THF})(\text{DBM})$ .** To a flask containing DBMH (42.8 g, 191.0 mmol) and 1000 mL of THF was added solid KH (7.70 g, 191.0 mmol). When the effervescence ceased, the solution was transferred to a dropping funnel and placed in the side neck of a three-neck 2-L flask containing  $\text{VCl}_3$  (30.0 g, 191.0 mmol) in 1000 mL of THF. The solution was refluxed for 2 h and cooled, and the THF solution of  $\text{K}^+\text{DBM}^-$  was added dropwise. The mixture was cooled and stirred overnight. The solution was filtered through Celite, and the solvent was removed by rotary evaporation to give a red-brown oil. Ether and a small amount of toluene were added. The flask was allowed to stand for a few hours, causing the oil to crystallize. The orange crystals were filtered off and washed with pentane. Yield 93 g, mp  $>300^\circ\text{C}$ .

Anal. Calcd for  $\text{VCl}_2\text{O}_3\text{C}_{19}\text{H}_{19}$ : C, 54.70; H, 4.59; O, 11.53. Found: C, 52.52; H, 4.69; O, 11.56.

**Preparation of  $\text{VCl}_2(\text{THF})_2(\text{acac})$ .** To a stirred suspension of  $\text{VCl}_3(\text{THF})_3$  (10.0 g, 26.8 mmol) in benzene was added, dropwise, 2,4-pentanedione (2.7 g, 26.8 mmol). The color rapidly turned yellow-brown. After stirring for 2 days the solution was filtered to give pale yellow crystals. The filtrate was stripped to dryness to give a further crop of yellow crystals. The analytical sample was recrystallized from THF to give pale green crystals. Yield 7.0 g (73%), mp 158–160  $^\circ\text{C}$ .

Anal. Calcd for  $\text{VCl}_2\text{O}_4\text{C}_{13}\text{H}_{23}$ : C, 42.76; H, 6.35. Found: C, 42.68; H, 6.39.

**Preparation of  $\text{CrCl}_2(\text{THF})_2(\text{DPM})$ .**  $\text{CrCl}_3(\text{THF})_3$  (7.0 g, 18.7 mmol) was suspended in benzene and, with stirring, DPMH (3.44 g, 18.7 mmol) was added dropwise. The color rapidly turned dark green, and after stirring for 2 h the solution was filtered and the benzene removed by rotary evaporation to give a green oil. A small amount of ether was added, followed by pentane, to precipitate light green crystals. Yield was 5.44 g (65%), mp 115–117  $^\circ\text{C}$ .

Anal. Calcd for  $\text{CrCl}_2\text{O}_4\text{C}_{19}\text{H}_{35}$ : C, 50.67; H, 7.83. Found: C, 49.58; H, 7.53.

**Preparation of  $\text{CrCl}_2(\text{THF})_2(\text{DBM})$ .** To a stirred solution of  $\text{CrCl}_3(\text{THF})_3$  (16.7 g, 44.6 mmol) in 200 mL of THF was added a solution of DBMH (10.0 g, 44.6 mmol) in THF. The solution rapidly turned green and, after stirring for 1 h, the solvent was removed by rotary evaporation to give a dark green oil. Benzene and a small amount of ether were added, causing the oil to crystallize. The crystals were then filtered off and washed with ether. Yield was quantitative (22 g), mp 119–120  $^\circ\text{C}$ .

Anal. Calcd for  $\text{CrCl}_2\text{C}_{23}\text{H}_{27}\text{O}_4$ : C, 56.33; H, 5.55; O, 13.05; Cr, 10.60. Found: C, 56.59; H, 5.62; O, 13.08; Cr, 9.37.

**Preparation of  $\text{CrCl}_2(\text{THF})_2(\text{acac})$ .** To a stirred solution of  $\text{CrCl}_3(\text{THF})_3$  (10.0 g, 26.7 mmol) in benzene was added acacH (2.67 g, 26.7 mmol). The solution rapidly turned green and deposited a green crystalline solid. After stirring overnight the solution was filtered and the solid washed with pentane. Yield 7.80 g (80%), mp 159–161  $^\circ\text{C}$ .

Anal. Calcd for  $\text{CrCl}_2\text{O}_4\text{C}_{13}\text{H}_{23}$ : C, 42.63; H, 6.33. Found: C, 42.51, 42.71; H, 6.43, 6.30.

**Preparation of  $\text{Ti}(\text{DPM})(o\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_2$ .**  $\text{TiCl}_2(\text{THF})_2(\text{DPM})$  (1.5 g, 3.36 mmol) was dissolved in ether and  $\text{Li-}o\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2$  (0.95 g, 7.72 mmol) was slowly added. The solution rapidly turned blue-green. After stirring for 0.5 h the solution was filtered and the

LiCl washed with ether. The solvent was removed by rotary evaporation and pentane was added. The solution was cooled to  $-40^{\circ}\text{C}$  for 24 h and filtered to give blue-green crystals. Yield 1.20 g (72%), mp  $68-75^{\circ}\text{C}$ .

Anal. Calcd for  $\text{TiO}_2\text{N}_2\text{C}_{29}\text{H}_{43}$ : C, 69.72; H, 8.68; N, 5.61; O, 6.40. Found: C, 68.46; H, 8.53; N, 7.63; O, 6.33.

**Preparation of  $\text{Ti}(\text{DPM})(o\text{-CH}_2\text{C}_6\text{H}_4\text{NMe}_2)_2$ .** To a stirred solution of  $\text{TiCl}_2(\text{THF})_2(\text{DPM})$  (4.1 g, 9.18 mmol) in ether was added  $\text{Li-}o\text{-CH}_2\text{C}_6\text{H}_4\text{NMe}_2$  (2.59 g, 18.4 mmol). The solution gradually turned dark green. After stirring for 1 h the solution was filtered, LiCl was washed with ether, and the solvent removed to give a fluffy green solid. The solid was dissolved in the minimum amount of pentane, filtered, and cooled to  $-40^{\circ}\text{C}$  for 6 days to give dark green crystals that were filtered off and dried in vacuo. Yield 2.8 g (61%). The crystals were decomposed upon standing at room temperature overnight and slowly decomposed at  $-30^{\circ}\text{C}$ .

Anal. Calcd for  $\text{TiO}_2\text{N}_2\text{C}_{29}\text{H}_{43}$ : C, 69.72; H, 8.68. Found: C, 68.90; H, 8.37.

**Preparation of  $\text{Cr}(\text{DPM})(o\text{-CH}_2\text{C}_6\text{H}_4\text{NMe}_2)_2$ .** To a stirred solution of  $\text{CrCl}_2(\text{THF})_2(\text{DPM})$  (3.0 g, 6.66 mmol) in ether was added  $\text{Li-}o\text{-CH}_2\text{C}_6\text{H}_4\text{NMe}_2$  (1.88 g, 13.32 mmol). The solution rapidly turned reddish brown. When all of the lithium alkyl had dissolved, the solution was filtered and the LiCl washed with ether. The ether was removed by rotary evaporation to give dark red-brown crystals that were washed from the flask with pentane. The yield was 1.32 g (40%), mp  $203-204^{\circ}\text{C}$ .

Anal. Calcd for  $\text{CrO}_2\text{N}_2\text{C}_{29}\text{H}_{43}$ : C, 69.15; H, 8.60; N, 5.56; O, 6.35. Found: C, 67.79; H, 8.65; N, 5.73; O, 6.33.

**Preparation of  $\text{V}(\text{DPM})(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_2$ .** To a solution of  $\text{VCl}_2(\text{THF})_2(\text{DPM})$  (5.0 g, 11.13 mmol) in ether was added, as a solid,  $\text{LiC}_6\text{H}_4\text{CH}_2\text{NMe}_2$  (3.14 g). The solution rapidly turned deep maroon. After stirring for 15 min the solution was filtered and the solid was removed by rotary evaporation to give a fluffy gum. Pentane was added to dissolve the solid, the solution was filtered and the flask was cooled to  $-30^{\circ}\text{C}$  overnight. Dark maroon crystals separated. They were filtered off and dried under vacuum. Yield was 2.5 g.

Anal. Calcd for  $\text{VO}_2\text{N}_2\text{C}_{29}\text{H}_{43}$ : C, 68.47; H, 9.71; N, 5.51; O, 6.29. Found: C, 68.12, 68.51, 68.04; H, 8.61, 8.69, 8.58; N, 5.52, 5.37; O, 7.06, 6.56.

**Attempted Preparation of  $\text{TiMe}_2(\text{DPM})(\text{PMe}_3)_2$ .** To a blue solution of  $\text{Ti}(\text{DPM})\text{Cl}_2(\text{PMe}_3)_2$  (1.0 g, 2.20 mmol) in ether was added 2.84 mL of a 1.55 M solution of methylolithium in ether at  $-78^{\circ}\text{C}$ . As the methylolithium was added, the solution turned reddish blue. After the addition was completed, the flask was gradually warmed to room temperature. At about  $-30^{\circ}\text{C}$  the color changed to green. After reaching room temperature the solution was filtered and the solvent was removed to give green crystals. Pentane was added, the solution was filtered again, and the pentane was removed to give another crop of green crystals. Yield 0.41 g, mp  $92-94^{\circ}\text{C}$ .

Anal. Calcd for  $\text{TiP}_2\text{O}_2\text{C}_9\text{H}_{19}$ : C, 55.20; H, 10.48; O, 7.74. Found: C, 58.42; H, 9.95; O, 8.60.

**Preparation of  $\text{Cr}(\text{DBM})(\text{Cp})\text{Cl}$ .** To a stirred suspension of  $\text{Cr}(\text{DBM})\text{Cl}_2(\text{THF})_2$  (3.0 g, 6.12 mmol) in THF was added solid  $\text{TiCp}$  (1.65 g, 6.12 mmol). The solution rapidly turned darker green and  $\text{TiCl}$  precipitated. The solution was stirred for 1 h, filtered, and evaporated to give dark green crystals. The crystals were dissolved in toluene, the solution was filtered, pentane was added, and the flask was cooled to  $-40^{\circ}\text{C}$  for overnight. The dark green crystals were filtered and washed with pentane. Yield 1.49 g (65%), mp  $255-260^{\circ}\text{C}$ .

Anal. Calcd for  $\text{CrO}_2\text{ClC}_{20}\text{H}_{16}$ : C, 63.92; H, 4.29; O, 8.52. Found: C, 63.53; H, 4.27; O, 9.97.

**Preparation of  $\text{Ti}(\text{DPM})(\text{HBpz}_3)\text{Cl}$ .** To a stirred solution of  $\text{TiCl}_2(\text{THF})_2(\text{DPM})$  (3.05 g, 6.72 mmol) in dichloromethane was added  $\text{KHBpz}_3$  (1.70 g, 6.72 mmol). The solution immediately turned deep blue. After stirring for 15 min the solution was filtered and the KCl washed with  $\text{CH}_2\text{Cl}_2$ . The solvent was removed by rotary evaporation to give deep blue crystals that were recrystallized from ether and pentane. Yield 3.0 g (93%), mp  $216-220^{\circ}\text{C}$ .

Anal. Calcd for  $\text{TiClO}_2\text{N}_6\text{BC}_{20}\text{H}_{29}$ : C, 50.08; H, 6.09; N, 17.53; O, 6.67. Found: C, 48.24; H, 6.01; N, 17.81; O, 4.52.

**Preparation of  $\text{Ti}(\text{DPM})(\text{PMe}_3)_2\text{Cl}_2$ .** To a stirred solution of  $\text{TiCl}_2(\text{THF})_2(\text{DPM})$  (3.0 g, 6.72 mmol) in ether was added  $\text{PMe}_3$  (1.02 g, 13.4 mmol). The solution rapidly turned dark blue. It was stirred for 15 min, filtered, and concentrated by rotary evaporation. Hexane was added to give a further crop of deep blue crystals. They

were filtered off and washed with pentane. Yield 2.25 g (74%), mp  $136-138^{\circ}\text{C}$ .

Anal. Calcd for  $\text{TiO}_2\text{Cl}_2\text{P}_2\text{C}_{17}\text{H}_{37}$ : C, 44.95; H, 8.21; O, 7.04. Found: C, 45.14; H, 8.06; O, 7.15.

**Preparation of  $\text{Cr}(\text{DPM})(\text{PMe}_3)_2\text{Cl}_2$ .**  $\text{PMe}_3$  (1.01 g, 13.4 mmol) was added to a stirred solution of  $\text{CrCl}_2(\text{THF})_2(\text{DPM})$  (3.0 g, 6.66 mmol) in ether. The color rapidly turned dark red-brown. After stirring for 1 h the solution was filtered and the solvent removed by rotary evaporation to give dark red crystals that were washed from the flask with pentane/ether (1:1 mixture). Yield 2.20 g, mp  $183-187^{\circ}\text{C}$ .

Anal. Calcd for  $\text{CrO}_2\text{Cl}_2\text{P}_2\text{C}_{17}\text{H}_{37}$ : C, 44.55; H, 8.14; O, 6.98. Found: C, 41.50; H, 7.87; O, 5.91.

**Preparation of  $\text{TiCl}_2(\text{DPM})(\text{bpy})$ .** To a stirred solution of  $\text{TiCl}_2(\text{DPM})(\text{THF})_2$  (3.0 g, 6.72 mmol) in ether was added a solution of 1.05 g of bipyridine. The solution turned to a very dark blue and a precipitate settled. After stirring overnight the solution was filtered and washed with ether. Yield was 3 g.

Anal. Calcd for  $\text{TiC}_{21}\text{H}_{27}\text{Cl}_2\text{N}_2\text{O}_2$ : C, 55.04; H, 5.94; N, 6.11; O, 6.98. Found: C, 56.22, 56.80; H, 5.85, 5.85; N, 5.77, 5.82; O, 4.23, 4.45.

**Preparation of  $\text{Li}^+[\text{N}(\text{SiMe}_3)_2]$ .** To a solution of hexamethyldisilazane (50.0 g, 0.309 mol) in 200 mL of hexane was added 194 mL of a 1.6 M solution of BuLi in hexane. When the addition was complete, the solution was stirred for 15 min and then stripped to dryness by rotary evaporation to give a quantitative yield of white crystals.

**Preparation of  $\text{Ti}(\text{DPM})[\text{N}(\text{SiMe}_3)_2]$ .** To a stirred solution of  $\text{TiCl}_2(\text{THF})_2(\text{DPM})$  (3.0 g, 6.72 mmol) in 100 mL of 50:50 ether/pentane was added solid  $\text{LiN}(\text{SiMe}_3)_2$  (2.25 g, 13.44 mmol). The solution rapidly turned dark blue. After stirring for 1 h the solution was filtered and LiCl washed with pentane and the solvent was removed by rotary evaporation to give dark blue crystals that may be recrystallized from pentane. Yield 3.10 g (83%), mp  $134-136^{\circ}\text{C}$ .

Anal. Calcd for  $\text{TiO}_2\text{N}_2\text{Si}_4\text{C}_{23}\text{H}_{55}$ : C, 49.87; H, 10.37; N, 5.06; O, 5.78. Found: C, 48.78; H, 9.61; N, 5.00; O, 4.44.

**Preparation of  $\text{Ti}(\text{DBM})[\text{N}(\text{SiMe}_3)_2]$ .** To a suspension of  $\text{TiCl}_2(\text{THF})_2(\text{DBM})$  (3.0 g, 6.17 mmol) in ether was added  $\text{LiN}(\text{SiMe}_3)_2$  (2.06 g, 12.34 mmol). The solution rapidly turned green. After stirring for 0.5 h the solution was filtered and the LiCl was washed with ether. The solvent was removed by rotary evaporation to give dark green crystals. They were dissolved in the minimum amount of pentane, filtered, and cooled to  $-40^{\circ}\text{C}$  for 24 h. The supernatant was decanted off, and the crystals were dried under vacuum. Yield 3.25 g (89%), mp  $134-138^{\circ}\text{C}$ .

Anal. Calcd for  $\text{TiO}_2\text{N}_2\text{Si}_4\text{C}_{23}\text{H}_{49}$ : C, 54.60; H, 8.32; N, 4.72; O, 5.39. Found: C, 54.41; H, 7.68; N, 4.25; O, 4.99.

**Preparation of  $\text{V}(\text{DPM})[\text{N}(\text{SiMe}_3)_2]$ .** To a stirred solution of  $\text{VCl}_2(\text{THF})_2(\text{DPM})$  (4.0 g, 8.90 mmol) in pentane was added  $\text{LiN}(\text{SiMe}_3)_2$  (2.97 g, 17.8 mmol). The solution rapidly turned deep red-purple. After stirring for 1 h the solution was filtered and the solvent removed by rotary evaporation to give red-purple crystals. Yield was 4.40 g (89%). The analytical sample was sublimed at  $10^{-4}$  mmHg and  $125^{\circ}\text{C}$ .

Anal. Calcd for  $\text{VO}_2\text{N}_2\text{Si}_4\text{C}_{23}\text{H}_{55}$ : C, 49.59; H, 10.31; N, 5.03. Found: C, 49.65; H, 9.79; N, 5.33.

**Preparation of  $\text{V}(\text{DBM})[\text{N}(\text{SiMe}_3)_2]$ .** To a stirred suspension of  $\text{V}(\text{DBM})\text{Cl}_2(\text{THF})_2$  (3.0 g, 6.13 mmol) in ether was added solid  $\text{LiN}(\text{SiMe}_3)_2$  (2.05 g, 12.3 mmol). The solution rapidly turned deep green. After stirring for 0.5 h, the solution was filtered. The LiCl was washed with ether, and the solvent was removed by rotary evaporation to give deep green crystals that may be recrystallized from pentane. Yield 3.50 g (96%), mp  $146-147^{\circ}\text{C}$ .

Anal. Calcd for  $\text{VO}_2\text{N}_2\text{Si}_4\text{C}_{23}\text{H}_{49}$ : C, 54.32; H, 8.27; N, 4.69; O, 5.36. Found: C, 54.29; H, 7.79; N, 4.65; O, 4.78. No ESR spectrum was obtained at  $-60^{\circ}\text{C}$ .

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**Registry No.**  $\text{TiCl}_2(\text{THF})_2(\text{DPM})$ , 65981-56-8;  $\text{TiCl}_2(\text{THF})_2(\text{DBM})$ , 65930-46-3;  $\text{TiCl}_2(\text{THF})_2(\text{acac})$ , 65930-45-2;  $\text{TiCl}_2(\text{DPM})_2$ , 65930-44-1;  $\text{VCl}_2(\text{THF})_2(\text{DPM})$ , 65930-43-0;  $\text{VCl}_2(\text{THF})_2(\text{DBM})$ , 65930-42-9;  $\text{VCl}_2(\text{THF})_2(\text{acac})$ , 61818-19-7;  $\text{CrCl}_2(\text{THF})_2(\text{DPM})$ , 65930-41-8;  $\text{CrCl}_2(\text{THF})_2(\text{DBM})$ , 65930-40-7;  $\text{CrCl}_2(\text{THF})_2(\text{acac})$ , 65930-50-9;  $\text{Ti}(\text{DPM})(o\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_2$ , 65930-48-5;  $\text{Ti}$

(DPM)(*o*-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>)<sub>2</sub>, 65930-47-4; Cr(DPM)(*o*-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>)<sub>2</sub>, 64061-49-0; V(DPM)(C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>, 61818-22-2; TiMe<sub>2</sub>(DPM)(PMe<sub>3</sub>)<sub>2</sub>, 65930-53-2; Cr(DBM)(Cp)Cl, 65930-52-1; Ti(DPM)(HBPz)<sub>2</sub>Cl, 65930-51-0; Ti(DPM)(PMe<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, 65930-49-6; Cr(DPM)(PMe<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, 65956-91-4; TiCl<sub>2</sub>(DPM)(bpy), 65930-54-3; Li<sup>+</sup>[N(SiMe<sub>3</sub>)<sub>2</sub>]<sup>-</sup>, 4039-32-1; Ti(DPM)[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, 61818-23-3; Ti(DBM)[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, 61818-24-4; V(DPM)[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, 61818-25-5; V(DBM)[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, 61818-26-6; TiCl<sub>3</sub>(THF)<sub>3</sub>, 18039-90-2; VCl<sub>3</sub>(THF)<sub>3</sub>, 19559-06-9; CrCl<sub>3</sub>(THF)<sub>3</sub>, 10170-68-0.

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## Mechanism and Steric Course of Octahedral Aquation. 19.<sup>1</sup> Aquation of a Labile Trans Isomer of the Dichloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Cation

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A new method for the synthesis of a labile form of *trans*-[Co(cyclam)Cl<sub>2</sub>]ClO<sub>4</sub> (cyclam = 1,4,8,11-tetraazacyclotetradecane) with the ligand in the *R,R,R,R(S,S,S,S)* configuration is reported. The kinetics and steric course of aquation are reported.  $k_{\text{aq}} = 1.75 \times 10^{-3} \text{ s}^{-1}$  at 25.0 °C,  $\Delta H^\ddagger = 24.2 \pm 0.5 \text{ kcal mol}^{-1}$ , and  $\Delta S^\ddagger = +9.9 \pm 1.6 \text{ cal K}^{-1} \text{ mol}^{-1}$  (0.0100 M HNO<sub>3</sub>,  $\mu = 1.00$  (NaNO<sub>3</sub>)). The immediate reaction product, a mixture of 75% *trans*- and 25% *cis*-[Co(cyclam)ClH<sub>2</sub>O]<sup>2+</sup> isomerizes to 100% *cis*-[Co(cyclam)ClH<sub>2</sub>O]<sup>2+</sup> with  $k_i = 1.3 \times 10^{-2} \text{ s}^{-1}$  at 25.0 °C,  $\Delta H^\ddagger = 25.8 \text{ kcal mol}^{-1}$ , and  $\Delta S^\ddagger = +19.3 \text{ cal K}^{-1} \text{ mol}^{-1}$ . The rate of aquation is independent of the acid concentration ( $[\text{H}^+] \geq 0.01 \text{ M}$ ) but is retarded by chloride. This is due to a reversible anation of the *trans*-[Co(cyclam)ClH<sub>2</sub>O]<sup>2+</sup> species which competes with the isomerization and which does not affect the *cis*-[Co(cyclam)ClH<sub>2</sub>O]<sup>2+</sup> species. The *R,R,R,R(S,S,S,S)* configuration of the ligand is retained throughout. This is the first example of an aquation of a complex with a macrocyclic tetraamine ligand that proceeds with stereochemical change.

### Introduction

Some years ago we examined the kinetics of aquation of a pair of *cis* and *trans* isomers of [Co(cyclam)Cl<sub>2</sub>]Cl (cyclam = 1,4,8,11-tetraazacyclotetradecane).<sup>2,3</sup> The *cis* species was some 10<sup>4</sup> times more labile than the *trans* isomer and it was remarked at the time that this was a most unusual observation for the noncatalyzed aquation reactions of cobalt(III) acido-amine complexes. However, it was pointed out that the ligand configuration (arising from the various possible combinations of the chiralities of the four secondary nitrogen atoms) was different in the two isomers and it was shown that the isomerization of the *cis* species to the more stable *trans* isomer required proton exchange and the inversion of configuration of two of the nitrogens.<sup>4</sup> Although there has been no direct structural determination there is good reason to believe that the stable *trans* isomer has the same meso configuration *R-3-S-2-S-3-R-2*<sup>5</sup> as in the Ni(II) complex, [Ni(cyclam)Cl<sub>2</sub>]<sup>7</sup> while the *cis* isomer is the racemic *R,R,R,R(S,S,S,S)* form. This ligand configuration was found recently in the [Co(cyclam)en]<sup>3+</sup> cation<sup>8</sup> (en = 1,2-diaminoethane) and, although the structure has never been formally published, it is reported in a footnote to another paper<sup>9</sup> that the *cis*-dichloro complex does indeed have the predicted structure. Although it is unlikely that the above *RSSR* form of the ligand can be folded without excessive strain to form the *cis* complex, the *R,R,R,R(S,S,S,S)* form of the ligand, despite remarks we have made to the contrary,<sup>10</sup> can be unfolded to give a somewhat strained *trans* complex which can retain the *gauche* conformations of the five-membered rings

but which requires the six-membered rings to be skew (Figure 1). Some 4 years ago, Cragel and Douglas<sup>11</sup> prepared an optically active isomer of *trans*-[Co(cyclam)Cl<sub>2</sub>]<sup>+</sup> by the action of methanolic hydrogen chloride on [Co(*R,R,R,R*-cyclam)-(C<sub>2</sub>O<sub>4</sub>)]<sup>+</sup> and they thought that the ligand might retain the *R,R,R,R* configuration throughout the reaction. The species was reported to be very labile, and our attempts to make it from racemic [Co(*R,R,R,R(S,S,S,S)*-cyclam)(C<sub>2</sub>O<sub>4</sub>)]Cl were unsuccessful, yielding only the *cis*-dichloro species. Recently we found that the new isomer could be obtained as a by-product in the preparation of *cis*-[Co(cyclam)Cl<sub>2</sub>]Cl from [Co(cyclam)(CO<sub>3</sub>)]Cl, but only in small yield and always in the presence of small quantities of the *trans*-[Co(*R,S,S,R*-cyclam)Cl<sub>2</sub>]<sup>+</sup> species. We now report a method in which the labile *trans*-dichloro complex is prepared directly from *cis*-[Co(*R,R,R,R(S,S,S,S)*-cyclam)Cl<sub>2</sub>]Cl under conditions that retain the configurations of the nitrogens and we also report the kinetics and steric course of the aquation. Busch et al. have recently described a series of dichloro complexes of cobalt(III) with macrocyclic tetraamines of various ring sizes<sup>12</sup> and in one case they report two configurational *trans* isomers. The aquation kinetics of these species have also been reported.<sup>13</sup>

### Experimental Section

**Preparation.** *trans*-Dichloro(*R,R,R,R(S,S,S,S)*)-1,4,8,11-tetraazacyclotetradecane]cobalt(III) Perchlorate. *cis*-[Co(cyclam)Cl<sub>2</sub>]Cl (1.9 g), prepared by the method of Poon and Tobe,<sup>3</sup> was added in small portions to 500 cm<sup>3</sup> of boiling absolute ethanolic hydrochloric acid (1 M) over a period of 1.5 h. After adding each portion it was advisable to wait until the color of the solution had changed from violet