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Paramagnetic Organometallic Compounds of the Early Transition Metals Stabilized by Chelating Benzyl and Phenyl Ligands

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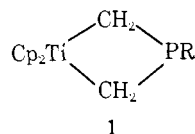
Contribution No. 2566 from the Central Research & Development Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898. Received April 17, 1978

Abstract: The reactions of $\text{LiCH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2$ and $\text{LiC}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2$ with Cp_2MCl ($\text{M} = \text{Ti, V, Sc}$; $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), CpTiCl_2 , CrCl_3 , and ScCl_3 led to the isolation of thermally stable, air-sensitive organometallic complexes whose stability is attributed to chelation. The reaction of $\text{CpTi}(\text{C}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2)_2$ with CO_2 leads to elimination of 1 equiv of *N,N*-dimethylbenzylamine and incorporation of CO_2 into the aromatic ring. The reaction of $\text{Cr}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_3$ with CO_2 gives a paramagnetic complex in which CO_2 has inserted into only one Cr-C bond and with diketones to give (diketonate) $\text{Cr}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_2$. The factors which contribute to the stabilization of paramagnetic organometallic compounds are discussed.

Introduction

The vast majority of organometallic compounds are diamagnetic.^{1,2} Little effort has been directed toward the synthesis of paramagnetic organometallic compounds because of the reactivity and instability of these compounds. The use of bulky alkyl substituents³⁻⁷ such as $-\text{CH}_2\text{SiMe}_3$, $-\text{CH}(\text{SiMe}_3)_2$, and $-\text{CMe}_3$ has yielded some very interesting and stable complexes. Recent work in our laboratory⁸⁻¹¹ as well as in others¹¹⁻¹² has shown that considerable stabilization can be achieved by the use of chelating organic ligands. For example, Brintzinger¹³ studied the reactions of alkyl Grignard reagents with Cp_2TiCl and found that the resulting paramagnetic compounds, $\text{Cp}_2\text{TiR}_2^-$, were very reactive and unstable at room temperature. In contrast, we found¹⁴ that the chelating lithium reagents

$\text{Li}(\text{CH}_2)_2\text{PR}_2$ reacted with Cp_2TiCl ,¹⁵ at room temperature, to give **1** as thermally stable, paramagnetic, crystalline solids.



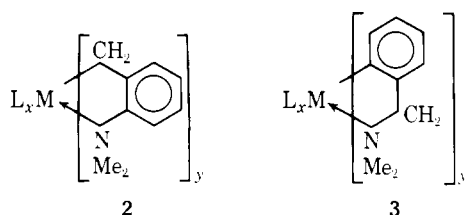
Similar compounds were isolated for vanadium and scandium. The stability of these complexes prompted us to examine, in greater detail, the stabilizing effect of chelating organic ligands. The work described in this paper is concerned with the preparation of compounds of the general types **2** and **3** (where $\text{M} = \text{Sc, Ti, V}$, and Cr ; $\text{L} = \text{Cp}$, diketone; $x = 0, 1, 2$; $y = 1-3$).

Table I. Electronic Spectra and Magnetic Moments for Paramagnetic Organometallic Complexes

compd ^a	solvent	electronic spectrum		magnetic moments	
		wavelength nm	extinction coefficient	solvent	$\mu_{eff}^{30^\circ}$
Cp ₂ V(C ₆ H ₄ CH ₂ NMe ₂)	THF	434	183	C ₆ H ₆	2.6
		514	140		
		683	161		
Cp ₂ Ti(C ₆ H ₄ CH ₂ NMe ₂)	THF	740	48	C ₆ B ₆	1.7
		635	45		
Cr(<i>p-t</i> -BuC ₆ H ₃ CH ₂ NMe ₂) ₃	THF	468	34	C ₆ H ₆	3.7
	CpTi(C ₆ H ₄ CH ₂ NMe ₂) ₂	C ₆ H ₅ Me	574	268	C ₆ H ₆
705			211		
Cr(CH ₂ C ₆ H ₄ NMe ₂) ₃	CH ₂ Cl ₂	656	80	CH ₂ Cl ₂	3.6
		745	84		
Cp ₂ V(CH ₂ C ₆ H ₄ NMe ₂)	C ₆ H ₅ Me	600	137	C ₆ H ₆	2.6
		715	131		
Cp ₂ Ti(CH ₂ C ₆ H ₄ NMe ₂)	C ₆ H ₅ Me	500	90	C ₆ H ₆	1.7
		717	49		
CpTi(CH ₂ C ₆ H ₄ NMe ₂) ₂	C ₆ H ₅ Me	615	210	C ₆ H ₆	1.6
		770	150		
Cr(DBM)(CH ₂ C ₆ H ₄ NMe ₂) ₂	CH ₂ Cl ₂	512	326	CH ₂ Cl ₂	4.1
Cr(acac)(CH ₂ C ₆ H ₄ NMe ₂) ₂	C ₆ H ₆	543	107	CH ₂ Cl ₂	4.1
Cr(O ₂ CCH ₂ C ₆ H ₄ NMe ₂)(CH ₂ C ₆ H ₄ NMe ₂) ₂	C ₆ H ₆	621	214	CH ₂ Cl ₂	4.0

^a DBM = anion of dibenzoylmethane; acac = anion of acetylacetonate; Cp = cyclopentadienide.

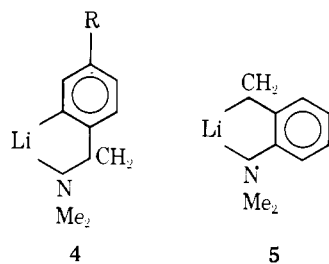
Compounds of type **3** are known for copper,¹⁶ cobalt,¹⁷ gold,¹⁸ silver,¹⁹ nickel,²⁰ palladium,²⁰ and platinum.²⁰ The coverage has now been extended to include chromium, titanium, vana-



dium, and scandium. Derivatives of the isoelectronic benzylchelated compound, **2**, have been prepared for the first time and are described in detail.

Results

A. Preparation of the Organolithium Reagents. The complexes described below were prepared from the lithium reagents **4** and **5**. The phenyllithium reagent has been prepared



previously under a variety of conditions.^{16,17,21} We have found that the most satisfactory procedure is to add an equimolar amount of *n*-butyllithium to an ether solution of *N,N*-dimethylbenzylamine. After 24 h, the white pyrophoric reagent, **4** (R = H), precipitates in essentially quantitative yield. It may then be filtered, washed with pentane, dried, and stored under a nitrogen atmosphere at room temperature. Starting with the substituted amine, **4** (R = -CMe₃) was prepared in good yield following the method of Cope and Gourley.¹⁷

The benzyllithium reagent, **5**, cannot be prepared in good yield from equimolar amounts of *N,N*-dimethyl-*o*-toluidine and *n*-butyllithium in refluxing hexane. However, in an ether/hexane mixture, **5** precipitated after 2 days at room

temperature as a pale yellow, ether-free pyrophoric solid. It may be separated by filtration, washed with pentane, dried, and stored under nitrogen at room temperature for several years without signs of decomposition. Metalation of the methyl group was confirmed by NMR and mass spectroscopy after deuterolysis which gave only Me₂NC₆H₄CH₂D. It is very soluble in tetrahydrofuran and insoluble in ether and hydrocarbon solvents.

B. Preparation of Cyclopentadienyl Transition Metal Derivatives. The addition of 1 molar equiv of **4** (R = H) to a suspension of Cp₂MCl¹⁵ (M = Ti, V, Sc) in ether gave an immediate precipitate of LiCl. After the solutions were stirred for a short time, they were filtered and the solvent was removed to give Cp₂M(C₆H₄-*o*-CH₂NMe₂) as very air-sensitive, crystalline solids. The titanium and vanadium compounds are paramagnetic (Table I) with magnetic moments (determined in solution²²) indicating one and two unpaired electrons per metal, respectively. Teuben et al.¹² have recently reported the preparations of the titanium and vanadium complexes as part of a study of the thermal stabilities of organometallic compounds.

The addition of LiCH₂C₆H₄-*o*-NMe₂ to a magnetically stirred suspension of Cp₂TiCl in ether, under a nitrogen atmosphere, gave a dark green solution from which Cp₂Ti(CH₂C₆H₄-*o*-NMe₂) was isolated as a dark green, very air-sensitive, crystalline solid. The magnetic moment, determined in benzene, was 1.7 μ_B. Deuterolysis of **2** gave *o*-Me₂NC₆H₄CH₂D. Similarly, Cp₂V(CH₂C₆H₄-*o*-NMe₂) was obtained as a very air-sensitive, green-brown, crystalline solid from the reaction of **5** with Cp₂VCl in ether. In contrast to Cp₂TiCH₂C₆H₅,²³ which decomposes at room temperature, it may be stored at room temperature for several days under nitrogen with no apparent decomposition. The vanadium complex is much less stable than the titanium complex and decomposes after several days at room temperature under a nitrogen atmosphere.

The ESR spectrum of Cp₂Ti(CH₂C₆H₄-*o*-NMe₂) is unusual in that it shows a doublet at *g* = 1.981 from coupling of the electron with one hydrogen atom ($\langle a_H \rangle$ = 5.1 G). The reason for the nonequivalence of the -CH₂-hydrogens is not clear but it may be due to steric interactions.²⁴

Green and Lucas²⁵ tried to prepare, without success, monocyclopentadienyl compounds CpTiR₂ by the reaction of [CpTiCl₂]_x²⁶ with the lithium or Grignard reagent of R. They

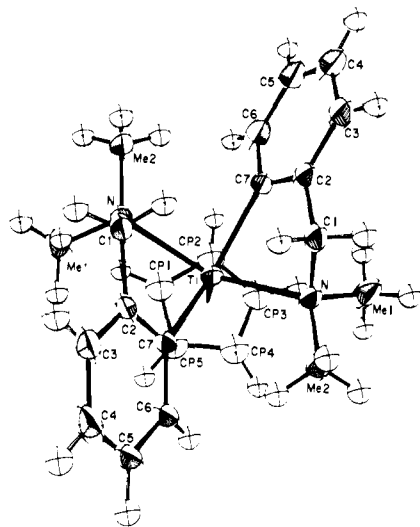
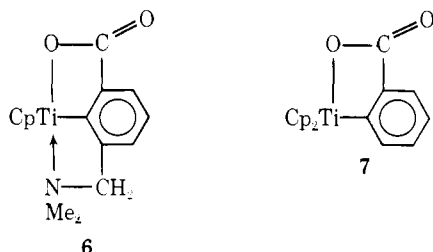
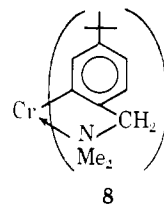


Figure 1. X-ray crystal structure of $\text{CpTi}(\text{C}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2)_2$.

found that disproportionation occurred to give Ti(II) and Ti(IV) compounds. In contrast, 2 equiv of **4** and **5** reacted smoothly with $[\text{CpTiCl}_2]_x$ in ether to give $\text{CpTi}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_2$ and $\text{CpTi}(\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_2$ as dark green, crystalline, very air-sensitive compounds. The magnetic moments of 1.6–1.7 μ_B , which were determined in benzene, are consistent with a d^1 electronic configuration. Both of these compounds should be stored under nitrogen at $<0^\circ\text{C}$ since decomposition occurs within a few days at room temperature. The X-ray crystal structure of $\text{CpTi}(\text{C}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2)_2$ has been determined⁸ and is reproduced in Figure 1. It is noteworthy that the two bidentate dimethylaminomethylphenyl ligands adopt roughly a trans configuration about titanium. The molecule has a 15-electron configuration and would be expected to form an adduct with a suitable donor ligand; however, we have found no interaction (by UV or ESR) with either trimethylphosphine or pyridine. When a solution of $\text{CpTi}(\text{C}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2)_2$ in toluene was heated to 74°C , under an atmosphere of dry CO_2 , the color changed from green to red-brown over 4 h and a rust-colored, crystalline compound precipitated. The solution was cooled and filtered, and the solid was washed with pentane. Analysis of the filtrate by GC/MS showed that $\text{C}_6\text{H}_5\text{CH}_2\text{NMe}_2$ was eliminated in this reaction. The elemental analysis and infrared spectrum, which shows a strong, sharp band at 1710 cm^{-1} , are consistent with **6**. The reaction is not unprecedented since Vol'pin and co-workers²⁷ found that reaction of CO_2 with $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_5)_2$ gave **7**, whose structure was determined by X-ray crystallography.



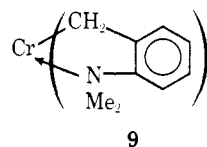
C. Reaction of MCl_3 ($\text{M} = \text{Ti}, \text{V}, \text{Sc}, \text{Cr}, \text{Fe}$). The addition of $\text{LiC}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2$ to a stirred suspension of CrCl_3 in tetrahydrofuran gave an orange suspension of $\text{Cr}(\text{C}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2)_3$. It was removed by filtration, washed with ethanol to remove LiCl , and then dried. It is stable and insoluble in CH_2Cl_2 , Me_2SO , DMF , H_2O , and nitromethane and decomposes only slowly in air. Because of its insolubility, we prepared the analogous *tert*-butyl substituted derivative, **8**. Unlike the unsubstituted chromium(III) organometallic, **8** is



soluble in ether and may be recrystallized from hot hexane. The magnetic moment is consistent with a d^3 electronic configuration.²⁸

The scandium compound $\text{Sc}(\text{C}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2)_3$ was prepared from ScCl_3 and $\text{LiC}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2$ in refluxing tetrahydrofuran and was obtained as a white, insoluble compound. Unlike the chromium analogue, it is pyrophoric in air and decomposes violently in CH_2Cl_2 and methanol.

The addition of 3 equiv of $\text{LiCH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2$ to a suspension of CrCl_3 in THF gave an immediate reaction and a dark orange solution from which dark red crystals of **9** were

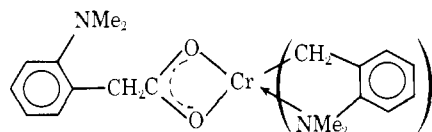


isolated in 83% yield. The analytical data, magnetic moment (3.6 μ_B), and mass spectrum, which showed a parent ion peak, are consistent with structure **9**. The benzyl compound is pyrophoric and soluble in CH_2Cl_2 , toluene, and tetrahydrofuran. The benzylscandium complex, $\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_3$, was prepared from anhydrous ScCl_3 and 3 equiv of $\text{LiCH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2$ in tetrahydrofuran and isolated as an extremely air-sensitive, pale yellow, crystalline solid. Crystallization and purification proved to be exceedingly difficult and the yield was 50–70%. The compound is diamagnetic and its NMR spectrum in benzene at room temperature showed equivalent N-Me resonances and a singlet for the benzylic hydrogens.

Unlike $\text{Cr}(\text{C}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2)_3$, **9** reacts with a variety of reagents containing acidic hydrogens. The addition of 1 molar equiv of a diketone to a suspension of $\text{Cr}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_3$ in benzene gave deep red solutions from which crystalline compounds of the composition (diketonate) $\text{Cr}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_2$ were isolated in good yield. They are much less air sensitive than the parent complex.

Triphenylsilanol reacted rapidly with a suspension of $\text{Cr}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_3$ in ether to give a dark blue solution from which a dark green solid was isolated. The analytical data and magnetic moment (determined in CH_2Cl_2) are consistent with the formulation $\text{Cr}[\text{OSi}(\text{C}_6\text{H}_5)_3]_3$. No reaction takes place between **9** and excess cyclopentadiene at room temperature after 24 h.

Carbon dioxide did not react rapidly with $\text{Cr}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_3$ under low pressure (15 psi) at room temperature in toluene. Upon raising the temperature to 75°C , the pressure rapidly decreased and a deep red solution resulted from which a dark red, crystalline material was isolated. The analytical data indicate that 1 equiv of CO_2 had been incorporated into the molecule. The magnetic moment of 4.0 μ_B is consistent with a d^3 ion in an octahedral environment. The infrared spectrum showed a strong, sharp band at 1532 cm^{-1} . Therefore structure **10** is proposed.



Despite several attempts, we were unable to isolate stable crystalline products from the reactions of VCl_3 , $\text{VCl}_3(\text{THF})_3$, TiCl_3 , $\text{TiCl}_3(\text{THF})_3$, and $\text{TiCl}_3(\text{NMe}_3)_2$ with **4** and **5** under a variety of conditions. The reaction of FeCl_3 with 3 equiv of $\text{LiC}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2$ in THF, at -80°C , gave a blood-red, crystalline precipitate. Upon warming the solution to room temperature the compound decomposed. Because of its thermal instability and insolubility, no further effort was made to purify and characterize the material.

Discussion

Organometallic compounds are well known for all of the transition metals^{1,2} and, by far, most of these compounds are diamagnetic. The reasons for the scarcity of paramagnetic organometallic compounds are twofold.

(1) The majority of research has focused on the preparation of diamagnetic organometallic compounds primarily because they are much easier to characterize and study by nuclear magnetic resonance spectroscopy. Paramagnetic organometallics generally do not exhibit sharp NMR spectra because of rapid electron spin relaxation. Their ESR spectra are generally broad and/or featureless and do not yield valuable structural information without detailed and time-consuming analysis. Characterization of paramagnetic organometallic molecules is based primarily on elemental analyses and magnetic susceptibility data, which can be extremely difficult to obtain because of the reactive nature of the compounds.

(2) Paramagnetic compounds are generally less stable and more reactive than their diamagnetic counterparts and, therefore, are more difficult to isolate. For example, the diamagnetic dihydrides of molybdenum and tungsten,²⁹ Cp_2MH_2 , are thermally stable and sublimable. Their isostructural paramagnetic analogues,³⁰⁻³² Cp_2NbH_2 and Cp_2TaH_2 , have only been characterized by ESR at low temperature and decompose on warming to room temperature.

We believe that there are three primary modes of decomposition for paramagnetic organometallic compounds which must be kinetically controlled or blocked to achieve stabilization. They are as follows.

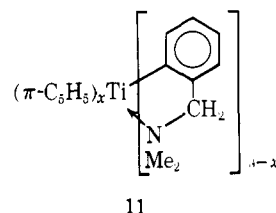
A. Oligomerization: $\text{R}_x\text{M} \rightarrow \text{R}_x\text{MMR}_x$. In the absence of steric effects, paramagnetic organometallic compounds tend to dimerize or oligomerize to minimize the electron spin on each metal center. This mode of decomposition is predominant in the chemistry of Re, Mo, W, and Cr.³² For example, $\text{Li}_2(\text{THF})_2\text{CrMe}_4$,³³ which is formally a d^4 complex, exists as a dimer with a quadruple bond postulated to account for the diamagnetism.

B. Disproportionation: $2\text{M}(y) \rightarrow \text{M}(y+1) + \text{M}(y-1)$. Disproportionation reactions are very common decomposition pathways. For example, Green and Lucas²⁵ tried to prepare, without success, monocyclopentadienyl compounds CpTiR_2 by the reaction of $[\text{CpTiCl}_2]_x$ with the lithium or Grignard reagents of R. They found that disproportionation occurred to give CpTiR_3 and uncharacterized Ti(II) compounds.

C. Homolysis: $\text{R}_x\text{M} \rightarrow \text{R}_{x-1}\text{M} + \text{R}$. Homolytic cleavage reactions of metal-carbon bonds are not well documented, although there is some evidence for this reaction in the chemistry of Mn(II) and Co(II).

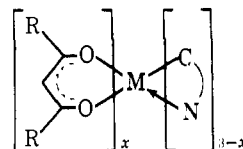
Oligomerization and disproportionation are decomposition modes controlled by both kinetic and thermodynamic factors; homolysis, principally by thermodynamic factors. The use of organic ligands with built-in donor atoms clearly enhances the thermal stability of paramagnetic organometallic molecules. The chelating group presumably inhibits mode (C) by tightly binding the alkyl or aryl group and inhibits (B) by supplying ligands to fill in the coordination sphere of the metal.

The presence of ligands which are capable of electron delocalization also enhances the thermal stability of paramagnetic organometallic molecules. For example, the stability of



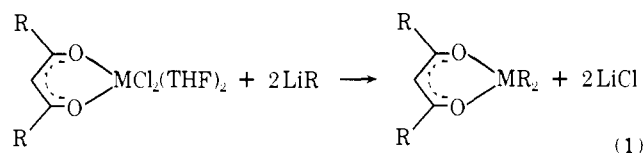
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compounds **11** dramatically increases as the number of cyclopentadienyl ligands increases from zero to two. This series is complicated by the different electron-donating contributions of the cyclopentadienyl and the *o*-aminophenyl ligand. Similarly, the diketonate ligand adds considerable stability to the series of compounds **12**. We were unable to isolate the tri-



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phenyl- and tribenzyl-chelated compounds for Ti and V because of their instability, yet the diketonate diorgano derivatives, **12** ($\text{M} = \text{Ti}, \text{V}$; $\text{R} = t\text{-Bu}$; $x = 1$), were sufficiently stable for isolation.^{9,34} They were prepared by reaction 1. The dike-



tonate and cyclopentadienyl ligands have the capability of delocalizing electron density from the metal center, thereby decreasing the radical nature of the metal center. We are in the process of calculating electron densities in these molecules by molecular orbital calculations and will report the results elsewhere.

We have prepared and characterized some interesting Cr(II) and Mn(II) derivatives²⁴ containing the dimethylaminomethylphenyl and 2-dimethylaminobenzyl ligands. Full details of that work will be reported later.

Catalytic Studies. Many of the compounds described in this paper are active coordination catalysts for the polymerization of olefins.³⁵ Full details of the polymerization studies will be published elsewhere.

Experimental Section

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

Elemental analyses were performed by the Physical and Analytical Division of the Central Research and Development Department and by Alfred Bernhardt (West Germany).

Cp_2TiCl , Cp_2VCl , and $\text{Cp}_2\text{ScCl}(\text{THF})$ were prepared by previously published methods.¹⁵

Preparation of $\text{LiC}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2$. A mixture of 135.2 g of *N,N*-dimethylbenzylamine and 625 mL of a 1.6 M solution of *n*-butyllithium in hexane in 1 L of diethyl ether was magnetically stirred overnight under a nitrogen atmosphere. A white solid precipitated. The flask was transferred to the drybox and the solution was filtered. The solid was washed with pentane and dried under vacuum. The yield of $\text{LiC}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2$ was 140 g (99%).

Preparation of $\text{Li-}t\text{-BuC}_6\text{H}_4\text{CH}_2\text{NMe}_2$. Fifty grams of *p*-(*tert*-butyl)benzylidimethylamine¹⁷ was added to 163 mL of a 1.6 M solution of *n*-butyllithium in hexane. The solution was refluxed under nitrogen for 16 h. It gradually turned orange and a white powder precipitated. The flask was then cooled and transferred to the drybox.

and the solid was filtered off and washed with pentane to give 46 g of a white solid (90%).

Preparation of $\text{Cp}_2\text{Sc}(\text{C}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2)$. To a suspension of $\text{Cp}_2\text{ScCl}(\text{THF})$ (3.0 g, 10.61 mmol) in ether was added $\text{LiC}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2$ (1.50 g). The solution was stirred for 30 min and filtered. Crystals separated immediately. The ether was concentrated by rotary evaporation, pentane was added, and the crystals were filtered off and washed with pentane. Yield was 87%, mp 150 °C.

Anal. Calcd for $\text{ScC}_{19}\text{H}_{22}\text{N}$: C, 73.77; H, 7.17; N, 4.53. Found: C, 72.74; H, 7.01; N, 4.38.

NMR ($\text{C}_6\text{D}_6/\text{Me}_4\text{Si}$): $\delta(\text{C}_5\text{H}_5) -5.95$, $\delta(\text{CH}_2) -3.23$, $\delta(\text{NMe}) -1.67$.

Preparation of $\text{Cp}_2\text{V}(\text{C}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2)$. To a suspension of Cp_2VCl (3.0 g, 13.8 mmol) in ether was added $\text{Li}[o\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2]$ (1.96 g, 13.8 mmol). The color rapidly turned dark green, and after stirring for 1 h the solution was filtered and the LiCl was washed with ether. The solvent was removed by rotary evaporation to give dark green crystals that were washed from the flask with pentane, yield 2.90 g (67%), mp 113–115 °C.

Anal. Calcd for $\text{VC}_{19}\text{H}_{22}\text{N}$: C, 72.37; H, 7.03; N, 4.44; V, 16.16. Found: C, 71.92; H, 6.83; N, 4.38; V, 17.02.

Preparation of $\text{Cp}_2\text{Ti}(\text{C}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2)$. Cp_2TiCl (3.0 g, 14.04 mmol) was suspended in ether and with stirring $\text{LiC}_6\text{H}_4\text{CH}_2\text{NMe}_2$ (1.98 g, 14.04 mmol) was added. The solution turned red-purple, and after stirring for 1 h it was filtered. The LiCl was washed with ether until the washings were colorless. The ether was reduced in volume to give mauve crystals which were filtered off and washed with pentane. The yield was 3.93 g (90%), mp 134–135 °C.

The analytical sample was recrystallized by dissolving a portion in the minimum volume of THF, followed by the addition of a small amount of ether and pentane. The flask was cooled at -40 °C for 12 h to give large, mauve crystals.

Anal. Calcd for $\text{TiC}_{19}\text{H}_{22}\text{N}$: C, 73.08; H, 7.10; N, 4.49; Ti, 15.34. Found: C, 72.71; H, 7.38; N, 4.51; Ti, 15.26.

Preparation of $\text{Sc}(\text{C}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2)_3$. Anhydrous scandium chloride (2.0 g, 13.2 mmol) was suspended in THF and $\text{LiC}_6\text{H}_4\text{CH}_2\text{NMe}_2$ (5.60 g, 39.6 mmol) was added as a solid. The solution was refluxed for 1 h and all of the solids were dissolved. The solution was then cooled and a white solid precipitated. It was filtered, then washed with THF and ether. The filtrate was stripped to dryness to give a white solid that was washed from the flask with THF, total yield 4.80 g (81%), mp 180–182 °C.

Anal. Calcd for $\text{ScC}_{27}\text{H}_{36}\text{N}_3$: C, 72.46; H, 8.11; N, 9.39. Found: C, 69.24; H, 7.96; N, 9.51.

Preparation of $\text{Cr}(\text{C}_6\text{H}_4\text{-}o\text{-CH}_2\text{NMe}_2)_3$. Anhydrous CrCl_3 (2.0 g, 12.63 mmol) was suspended in 100 mL of THF and solid $\text{LiC}_6\text{H}_4\text{CH}_2\text{NMe}_2$ (5.72 g, 37.8 mmol) was added. An orange solid precipitated, and after stirring for 1 h the solid was filtered off and washed with THF, ethanol, ether, and pentane. The yield was quantitative. The compound was insoluble in CH_2Cl_2 , Me_2SO , DMF, and nitromethane and decomposed in the air within 1 h.

Anal. Calcd for $\text{CrC}_{27}\text{H}_{36}\text{N}_3$: C, 71.33; H, 7.98; N, 9.25. Found: C, 70.30; H, 7.90; N, 9.21.

Preparation of $\text{Cr}(t\text{-Bu-C}_6\text{H}_3\text{-CH}_2\text{NMe}_2)_3$. Anhydrous CrCl_3 (2.0 g, 12.63 mmol) was suspended in 200 mL of ether and, with stirring, $\text{Li}(t\text{-Bu-C}_6\text{H}_3\text{CH}_2\text{NMe}_2)$ (7.48 g, 37.8 mmol) was added. The CrCl_3 rapidly dissolved to give an orange solution. After stirring for 2 h, the solution was filtered and the lithium chloride was washed with ether. The ether was then removed by rotary evaporation to give an orange oil. The addition of pentane caused crystals to form so the flask was cooled at -40 °C for 2 h and the crystals were filtered off. The yield was 66%, mp 224–225 °C.

The analytical sample was recrystallized by dissolving a sample in boiling hexane and cooling at -40 °C for 24 h. The orange crystals were filtered off and dried in vacuo.

Anal. Calcd for $\text{CrC}_{39}\text{H}_{60}\text{N}_3$: C, 75.19; H, 9.71; N, 6.75; Cr, 8.35. Found: C, 75.79; H, 9.63; N, 6.81; Cr, 7.63.

Preparation of $\text{Li}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)$. To a stirred solution of *o*-,*N*-dimethylaminotoluene (96.0 g, 0.71 mol) in 300 mL of hexane and 50 mL of ether was added 444 mL of a 1.6 M solution of BuLi in hexane. The solution was stirred at room temperature for 2 days to give yellow crystals. The solid was filtered off in the box and washed with pentane. Yield was quantitative, mp >200 °C.

Preparation of $\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_3$. To a suspension of anhydrous ScCl_3 (2.0 g, 13.2 mmol) in THF was added $\text{LiCH}_2\text{C}_6\text{H}_4\text{NMe}_2$ (5.60 g, 39.6 mmol). The solution was stirred overnight to give a deep

orange-yellow solution. The THF was stripped off to give an oil that was dissolved in toluene and filtered, and the toluene was stripped off. Ether was added and a flask was agitated for several minutes to give large, pale yellow crystals. The crystals were filtered off and washed with pentane, yield 3.30 g (56%), mp 115–118 °C.

Anal. Calcd for $\text{ScC}_{27}\text{H}_{36}\text{N}_3$: C, 72.45; H, 8.11; N, 9.39. Found: C, 70.72; H, 8.05; N, 9.56.

NMR (220 MHz) $\text{C}_6\text{D}_6/\text{Me}_4\text{Si}$: $\delta(\text{CH}_2) -1.64$, $\delta(\text{NMe}) -2.27$.

Preparation of $\text{Cr}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_3$. To a stirred suspension of CrCl_3 (3.15 g, 19.9 mmol) in THF was added $\text{LiCH}_2\text{C}_6\text{H}_4\text{NMe}_2$ (8.47 g, 60.0 mmol). The solution became warm and turned dark orange. After stirring for 15 min the solvent was evaporated and the solids were washed from the flask with ether. The dark red crystals were dissolved in CH_2Cl_2 and filtered through Celite, and the LiCl was washed with CH_2Cl_2 until the washings were colorless. The CH_2Cl_2 was evaporated to give dark red crystals that were washed from the flask with ether, yield 7.50 g (83%), mp 167–168 °C.

Anal. Calcd for $\text{CrC}_{27}\text{H}_{36}\text{N}_3$: C, 71.33; H, 7.98; N, 9.25. Found: C, 70.05; H, 7.93; N, 9.92.

Preparation of $\text{Cp}_2\text{V}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)$. To a solution of Cp_2VCl (3.0 g, 13.8 mmol) in ether was added $\text{LiCH}_2\text{C}_6\text{H}_4\text{NMe}_2$ (1.96 g, 13.8 mmol). The solution gradually turned green-brown, and after stirring for 1 h it was filtered. The ether was removed to give green-brown crystals that were washed from the flask with pentane. The pentane filtrate was cooled to -40 °C for several hours to give a further crop of green-brown crystals, yield 3.85 g (80%), mp 67–70 °C.

Anal. Calcd for $\text{VC}_{19}\text{H}_{22}\text{N}$: C, 72.37; H, 7.03; N, 4.44. Found: C, 71.68; H, 7.02; N, 5.05.

Preparation of $\text{Cp}_2\text{Ti}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)$. To a stirred suspension of Cp_2TiCl (3.02 g, 14.2 mmol) in 150 mL of ether was added solid $\text{Li}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2)$ (2.0 g, 14.2 mmol). The solution was magnetically stirred for 1 h, then filtered to give a green solution. The solids on the filter were washed with benzene until the washings were colorless, then the volume was reduced by rotary evaporation. Pentane was added, the flask was cooled to about -20 °C, and the green crystals were filtered, washed with pentane, and dried. Yield was 4.20 g (95%), mp 154–155 °C.

Anal. Calcd for $\text{TiC}_{19}\text{H}_{22}\text{N}$: C, 73.08; H, 7.10; N, 4.49; Ti, 15.34. Found: C, 72.21; H, 7.05; N, 4.65; Ti, 15.94.

ESR (in toluene at 35 °C) $g = 1.981$; (a_{H}) 5.1 G, (a_{Ti}) 7.2 G.

Preparation of $\text{CpTi}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_2$. To a stirred suspension of $[\text{TiCpCl}_2]_x$ (2.0 g, 10.9 mmol) in ether was added solid $\text{LiCH}_2\text{C}_6\text{H}_4\text{NMe}_2$ (3.07 g, 21.8 mmol). The solution was stirred for 4 h to give a dark green color, then filtered. The solvent was removed by rotary evaporation to give a dark green, sticky solid. Pentane was added, and after 1 h the solution was filtered to give 2.0 g of dark green crystals. The green pentane solution was cooled to -40 °C to give 0.43 g of dark crystals, total yield 59%, mp 118–125 °C.

Anal. Calcd for $\text{TiN}_2\text{C}_{23}\text{H}_{29}$: C, 72.43; H, 7.66; N, 7.35. Found: C, 71.56; H, 7.65; N, 7.15.

ESR spectrum (toluene, -60 °C): $g = 1.977$.

Preparation of $\text{CpTi}(\text{O}_2\text{C})\text{C}_6\text{H}_3\text{-}o\text{-CH}_2\text{NMe}_2$. A solution of $\text{CpTi}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_2$ (1.04 g) in 25 mL of toluene was heated to 74 °C in a pressure bottle under an atmosphere of dry CO_2 at 15 psi. The solution gradually turned from green to red-brown over 4 h and a rust-colored, crystalline compound separated. The solution was cooled and filtered, and the solid was washed with pentane, mp 179–181 °C.

Anal. Calcd for $\text{TiO}_2\text{NC}_{15}\text{H}_{16}$: C, 61.86; H, 5.88; N, 4.81; Ti, 16.44. Found: C, 61.82; H, 6.00; N, 5.10; Ti, 17.20.

IR (Nujol) shows a broad peak at 1710 cm^{-1} . ESR (toluene, room temperature): $g = 1.979$; (a_{Ti}) = 12.6 G.

Preparation of $\text{Cr}(\text{DBM})(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_2$. To a stirred suspension of $\text{Cr}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_3$ (1.5 g, 3.30 mmol) in benzene was added dibenzoylmethane (0.74 g, 3.30 mmol). The solution became deep red, and after stirring for 30 min it was filtered and the benzene was removed to give a red oil. Ether was added and the flask was set aside for 10 min. Large red crystals separated. They were filtered off and washed with pentane. Yield was 1.38 g (78%), mp 197–198 °C.

Anal. Calcd for $\text{CrC}_{33}\text{H}_{35}\text{N}_2\text{O}_2$: C, 72.89; H, 6.49; N, 5.15; O, 5.89. Found: C, 71.99; H, 72.50; N, 71.92; H, 6.43; O, 6.59; N, 4.97; O, 6.12; O, 6.16.

Preparation of $\text{Cr}(\text{acac})(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_2$. To a stirred suspension of $\text{Cr}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_3$ (1.5 g, 3.30 mmol) in benzene

was added acetylacetone (0.33 g, 3.30 mmol). The solution became deep red-purple. After stirring for 1 h the solution was filtered and the benzene was removed by rotary evaporation to give a deep red oil. Pentane was added and the flask was cooled to -40°C overnight to give dark red crystals that were filtered off and dried. Yield was 70%, mp 138–140 $^{\circ}\text{C}$.

Anal. Calcd for $\text{CrC}_{23}\text{H}_{31}\text{N}_2\text{O}_2$: C, 65.85; H, 7.45; N, 6.68; O, 7.63. Found: C, 64.75, 64.45, 65.18; H, 7.30, 7.46, 7.74; N, 6.40, 6.49; O, 7.82, 7.71.

Preparation of $\text{Cr}(\text{O}_2\text{CCH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_2$. A pressure bottle containing $\text{Cr}(o\text{-CH}_2\text{C}_6\text{H}_4\text{NMe}_2)_3$ (1.50 g, 3.30 mmol) dissolved in 30 mL of toluene was evacuated and pressurized to 15 psi with CO_2 . No reaction occurred at ambient temperature so the solution heated to 75°C . The pressure rapidly dropped and the solution became deep red. The solution was cooled, transferred to the box, and filtered. The solvent was removed to give a deep red oil. It was dissolved in ether, pentane was added, and the flask was cooled to give dark red crystals that were filtered off and washed with pentane. Yield was 88%, mp 110–112 $^{\circ}\text{C}$.

Anal. Calcd for $\text{CrC}_{28}\text{H}_{36}\text{N}_3\text{O}_2$: C, 67.44; H, 7.78; N, 8.43; Cr, 10.43. Found: C, 67.27; H, 6.85; N, 8.63; Cr, 10.65.

Preparation of $\text{Cr}(\text{OSiPh}_3)_3$. Triphenylsilanol (2.08 g, 7.53 mmol) was added to a suspension of $\text{Cr}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2)_3$ (1.14 g, 2.51 mmol) in ether. The solution turned deep blue, and after 30 min it was filtered and the ether was removed to give a green oil. A small amount of ether was added to dissolve the oil, pentane was added, and the flask was cooled to -40°C . Green crystals separated; they were filtered off and washed with pentane. Yield was 1.97 g, mp 112–115 $^{\circ}\text{C}$.

Anal. Calcd for $\text{CrO}_3\text{Si}_3\text{C}_{54}\text{H}_{45}$: C, 73.85; H, 5.16; O, 5.47; Cr, 5.92. Found: C, 71.57; H, 5.45; O, 6.81; Cr, 6.15.

Electronic spectrum (C_6H_6): 438 nm (ϵ 89), 862 (120).

Magnetic moment (CH_2Cl_2): $\mu_{\text{eff}} = 3.7 \mu_{\text{B}}$.

Preparation of $\text{CpTi}(\text{O}_2\text{C})\text{C}_6\text{H}_3\text{CH}_2\text{NMe}_2$. A solution of $\text{CpTi}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_2$ (1.04 g) in 25 mL of toluene was heated to 74°C in a pressure bottle under an atmosphere of dry CO_2 at 15 psi. The solution gradually turned from green to red-brown over a period of 4 h and a rust-colored, crystalline compound separated. The solution was cooled and filtered and the solid was washed with pentane, mp 179–181 $^{\circ}\text{C}$.

Anal. Calcd for $\text{TiO}_2\text{NC}_{15}\text{H}_{17}$: C, 61.86; H, 5.88; N, 4.81; Ti, 16.44. Found: C, 61.82; H, 6.00; N, 5.10; Ti, 17.20.

IR (Nujol) shows a broad peak at 1710 cm^{-1} .

ESR (toluene, room temperature): $g = 1.979$; $(a_{\text{Ti}}) = 12.6 \text{ G}$.

Acknowledgments. I am grateful to Dr. P. Krusic for re-

cording some of the ESR spectra and to Dr. G. W. Parshall for helpful discussions.

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