Table I. Product Yields in Preparation of [M(L- or D-asp)(L-his)] and $[M(L\text{-asp})_2]^-$ (M = Cr, Co)

	[Co(L-asp)-(L-his)]	[Cr(L-asp)-(L-his)]
trans(O_5),cis(N_5)	0.53	0.61
cis(O_5),trans(N_5)	0.06	0.02
L-*fac*	0.41	0.37
	[Co(D-asp)-(L-his)]	**[Cr(D-asp)-(L-his)]**
cis(O_5),cis(N_5)	0.48	0.58
trans(O_5),trans(N_5)	0.01	trace
D-*fac*	0.51	0.42
	$[Co(L\text{-asp})_2]^-$	**$[Cr(L\text{-asp})_2]^-$**
trans(N_5)	0.26	0.33
cis(N_5),trans(O_5)	0.47	0.40
cis(N_5),trans(O_5)	0.27	0.27

of elution and the elution intervals among Cr(III) complexes with those for Co(III) complexes.

For the case of Cr(III) complexes having these ligands, difficulty of characterization arises since no information is obtainable from their ^1H NMR spectra. By comparing the CD spectra of the [Cr(L- or D-asp)(L-his)] complexes with those of the [Co(L- or D-asp)(L-his)] complexes, we found a similarity in their CD spectra between the second-absorption-band region and the higher energy side of the first-absorption-band region. This similarity must serve for the characterization of the isomers of $[Cr(L\text{-asp})_2]^-$. Figure 7a shows that the first eluate (B) of the Cr(III) complexes has one CD peak in the first absorption region and one in the second absorption region, while the first eluate isomer (F) of the Co(III) complexes has two peaks in the first absorption region. In comparison of these two CD spectra between the higher energy side region of the first absorption and the second absorption region, the sign (positive at 20 and 27 × 10^3 cm^{-1}) is found to be the same. As is shown in Figure 7b the second eluate isomer(C) of the Cr(III) complexes has two positive peaks in the first-absorption-band region and one positive in the second-absorption-band region. On the other hand, three peaks (negative, positive, positive in order of energy increase) appear for the second eluate of $[Co(L\text{-asp})_2]^-$. Good agreement concerning their signs are obtained between the higher energy side of the first-absorption-band region and the second absorption band. For both of the third eluates (Figure 7c), similarity of those CD spectra seems to exist in the whole region outside the charge-transfer-band region, though the intensity of the CD spectrum of the third eluate D isomer of the $[Cr(L\text{-asp})_2]^-$ complexes at the second-absorption-band region is slightly smaller than that for the third isomer of the $[Co(L\text{-asp})_2]^-$ complexes. Therefore the similarity of the CD spectra between the higher energy side of the first-absorption-band region and the second-absorption-band region may be used to assign isomer B as trans(N_5),cis(O_5), isomer C as cis(N_5),trans(O_5), and isomer D as cis(N_5),trans(O_6).

In comparison of the CD spectra of the $[Cr(L\text{-asp})_2]^-$ complexes with those of the $[Co(L\text{-asp})_2]^-$ complexes in the charge-transfer region, surprisingly great differences are seen in their peak maxima and their signs.

Distributions of the isomers obtained here are listed in Table I together with those of the corresponding Co(III) complexes. The distributions of the [Cr(L- or D-asp)(L-his)] complexes are quite similar to those of the [Co(L- or D-asp)(L-his)] complexes and indicate that factors affecting the instabilities of these complexes such as steric hindrance and/or electronic effects are similar for both metal ions.

Registry No. CL1, 78685-02-6; CD1, 78685-03-7; CL3, 78638-59-2; CD3, 78684-38-5; B, 78684-39-6; C, 78656-76-5; D, 78684-40-9.

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Reaction of Metallocene Dichlorides of Titanium(IV) and Zirconium(IV) with Lithium Bis(trimethylsilyl)amide

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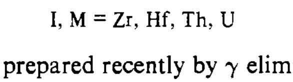
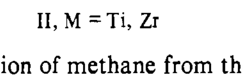
Reaction of Cp_2TiCl_2 with 1 or 2 molar equiv of $LiN(SiMe_3)_2$ yields the previously described metallacycle $Cp_2\overline{TiCH_2SiMe_2N}SiMe_3$. Mass balance shows that for each mole of metallacycle formed, 1 molar equiv of hydrogen chloride is also formed. The related zirconium metallacycle was prepared from $Cp_2Zr(H)(Cl)$ and $LiN(SiMe_3)_2$. The bis(silylamide) of zirconium, $Cp_2Zr[N(SiMe_3)_2]_2$, was prepared from Cp_2ZrCl_2 and 2 molar equiv of $LiN(SiMe_3)_2$. The Me_3Si groups in the latter compound are magnetically nonequivalent at 27 °C but coalesce at 84 °C on the ^1H NMR time scale.

The four-membered-ring heterocyclic molecules (I) have



I, M = Zr, Hf, Th, U



II, M = Ti, Zr

been prepared recently by γ elimination of methane from the tris(silylamido) alkyls as shown in eq 1.[1] A related metallacycle II, M = Ti, was isolated some years ago in the reaction

$$[(Me_3Si)_2N]_3MMe \xrightarrow{\Delta} I + MeH \qquad (1)$$

of dicyclopentadienyltitanium dichloride and 2 molar equiv of lithium bis(trimethylsilyl)amide.[2] It was implicitly suggested that the γ-hydrogen atom of a bis(trimethylsilyl)amido group in hypothetical $Cp_2Ti[N(SiMe_3)_2]_2$ was eliminated as $(Me_3Si)_2NH$, since the latter molecule was detected. Later, an explicit mechanism was proposed that suggested lithium bis(trimethylsilyl)amide deprotonates a γ-methyl group of the coordinated silylamide ligand in hypothetical $Cp_2Ti[N(SiMe_3)_2](Cl)$, yielding $Li\{Cp_2Ti[N(SiMe_3)(SiMe_2CH_2)](Cl)\}$ and $(Me_3Si)_2NH$. The former ion pair then eliminates lithium chloride, yielding II, M = Ti.[3a] To confuse the matter further,

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it is said that Me_3SiCl is eliminated.[3b]

Since we have never observed the coordinated $(Me_3Si)_2N$ group to act as a hydrogen atom acceptor, though this is a well-known reaction in organic chemistry,[4] we decided to carefully reexamine this reaction in some detail with respect to its stoichiometry.

Addition of 2 molar equiv of lithium bis(trimethylsilyl)amide to dicyclopentadienyltitanium dichloride in either pentane or diethyl ether yielded the metallacycle II, M = Ti, after sublimation [100–110 °C (10^{-3} mm)] and ca. 1 molar equiv of unreacted lithium bis(trimethylsilyl)amide, isolated by crystallization. The spectroscopic properties of II, M = Ti, given in the Experimental Section (including the proton-coupled ^{13}C NMR spectrum) are in agreement with those previously given.[2] Reaction of dicyclopentadienyltitanium dichloride and 1 molar equiv of lithium bis(trimethylsilyl)amide in pentane or diethyl ether also yields metallacycle II, M = Ti, and hydrogen chloride after vacuum sublimation. Thus, at room temperature, Cp_2TiCl_2 (19.2 mmol) reacts with $LiN(SiMe_3)_2$ (19.3 mmol) presumably to give $Cp_2Ti(Cl)[N(SiMe_3)_2]$ though this was not isolated. The chloro amide then yields the metallacycle II, M = Ti (13.0 mmol), and HCl (15.6 mmol) after vacuum sublimation (see Experimental Section for details concerning the mass balance). Thus, the 1:1 molar relationship is clearly established. The formation of $(Me_3Si)_2NH$, previously described,[2] is probably due to reaction of excess lithium bis(trimethylsilyl)amide and hydrogen chloride. The detailed mechanism of this γ-hydrogen chloride elimination, though not the stoichiometry, is obscure.

Reaction of the zirconium analogue, Cp_2ZrCl_2, with lithium bis(trimethylsilyl)amide takes a different course. Addition of 2 molar equiv of lithium bis(trimethylsilyl)amide to dicyclopentadienylzirconium dichloride in diethyl ether yields the bis(silylamide), $Cp_2Zr[N(SiMe_3)_2]_2$. The cyclopentadienyl rings are equivalent in the ^1H and $^{13}C\{^1H\}$ NMR spectra, but the trimethylsilyl groups are nonequivalent at 27 °C, since two equal-area resonances are observed for the silylamide hydrogen and carbon atoms. Thus, the four Me_3Si groups are orientated such that they are pairwise inequivalent. This type of inequivalence of $(Me_3Si)_2N$ groups is well-known in the solid state.[5]

A variable-temperature ^1H NMR experiment shows that the trimethylsilyl groups coalesce at 84 °C. The barrier to rotation, most reasonably ascribed to severe steric congestion about the zirconium atom, is slow on the ^1H NMR time scale at room temperature though fast at temperatures greater than 85 °C. Line-shape analysis[6] yields a barrier ($\Delta G^{\ddagger}_{T_c}$) of 18 kcal mol^{-1}.

The zirconium metallacycle (II, M = Zr) can be prepared by allowing dicyclopentadienylzirconium hydrochloride to react with 1 molar equiv of lithium bis(trimethylsilyl)amide at room temperature in diethyl ether. The γ-hydrogen elimination is facile, since we could see no evidence in the ^1H NMR or infrared spectra of the crude reaction product for a hydride-containing species. This conclusion is in accord with the metalation processes described earlier.[1]

Experimental Section

All reactions were performed under argon. Analyses were done by the microanalytical laboratory of this department. Proton and carbon nuclear magnetic resonance spectra were obtained at 89.56 and 22.50 MHz, respectively, on a JEOL FX90Q spectrometer. Chemical shifts are reported in δ units (Me_4Si = 0), positive values being to high frequency. Room-temperature spectra were obtained on benzene-d_6 solutions, and variable-temperature spectra were measured on toluene-d_8 solutions.

Preparation of $Cp_2\overline{TiCH_2SiMe_2N}SiMe_3$. (a) From 2 Molar Equiv of $LiN(SiMe_3)_2$. A suspension of dicyclopentadienyltitanium dichloride[7] (1.8 g, 0.0072 mol) and lithium bis(trimethylsilyl)amide [prepared by heating (75 °C) a melt of $LiN(SiMe_3)_2 \cdot 2OEt_2$ under low pressure (10^{-2} mm) until sublimation was evident] (2.4 g, 0.014 mol) in pentane (100 mL) was stirred at room temperature for 24 h. The resulting red solution was filtered, and the filtrate was concentrated under reduced pressure to ca. 30 mL and cooled (−20 °C). The white blocks were collected, dried under vacuum, and identified as $LiN(SiMe_3)_2$ by ^1H NMR and a melting point of 70–72 °C (lit.[8] mp 71–72 °C); yield 1.4 g (0.0084 mol; 58%). The pentane was removed under reduced pressure from the filtrate to yield a red, gummy residue, which yielded the metallacycle on sublimation [110–120 °C (10^{-3} mm)] in 49% (1.2 g) yield as a red, waxy solid. The ^1H NMR spectrum consisted of a singlet at δ 5.86 due to Cp_2Ti, a singlet at δ 3.14 due to $\overline{TiCH_2SiMe_2N}SiMe_3$, a singlet at δ 0.11 due to $\overline{TiCH_2SiMe_2N}SiMe_3$, and a singlet at δ −0.05 due to $\overline{TiCH_2SiMe_2N}SiMe_3$ in an area ratio of 10:2:9:6. The ^{13}C NMR spectrum consisted of a doublet centered at δ 113.7 (J_{CH} = 174 Hz) due to Cp_2Ti, a triplet centered at δ 71.3 (J_{CH} = 123 Hz) due to $TiCH_2$, a quartet centered at δ 4.42 (J_{CH} = 117 Hz) due to Me_3SiN, and a quartet centered at δ 2.05 (J_{CH} = 118 Hz) due to Me_2Si.

(b) From 2 Molar Equiv of $LiN(SiMe_3)_2 \cdot 2OEt_2$. The lithium bis(trimethylsilyl)amide–bis(diethyl ether) complex (3.7 g, 0.012 mol) in diethyl ether (100 mL) was added to a suspension of dicyclopentadienyltitanium dichloride (1.5 g, 0.0058 mol) in diethyl ether (60 mL). The red suspension was stirred at room temperature for 16 h and then filtered. Diethyl ether was evaporated from the filtrate, and the residue was exposed to vacuum for 4 h at 50 °C. The residue was extracted with pentane (3 × 40 mL), and the extract was concentrated to ca. 30 mL under reduced pressure and cooled (−20 °C). The large, colorless blocks were isolated and shown to be $LiN(SiMe_3) \cdot 0.5OEt_2$ by ^1H NMR (1.1 g, 0.0054 mol). The red mother liquor was taken to dryness, and sublimation [110–120 ° C (10^{-3} mm)] yielded the metallacycle in 62% (1.2 g) yield.

(c) From 1 Molar Equiv of $LiN(SiMe_3)_2 \cdot 2OEt_2$. Lithium bis(trimethylsilyl)amide–bis(diethyl ether) (2.8 g, 0.0089 mol) in diethyl ether (60 mL) was added to dicyclopentadienyltitanium dichloride (2.2 g, 0.0088 mol) in diethyl ether (100 mL). The suspension was stirred to room temperature (16 h) and filtered, and diethyl ether was removed under reduced pressure. The residue was exposed to vacuum for 5 h (50 °C) and then extracted with pentane (2 × 50 mL). The combined extracts were concentrated to ca. 10 mL and cooled (−20 °C) to give $LiN(SiMe_3)_2 \cdot 0.5OEt_2$ (0.20 g, 0.00098 mol). The mother liquor was evaporated to dryness, and sublimation afforded the metallacycle in 71% (2.1 g) yield.

For an investigation of the stoichiometry of the reaction, $LiN(SiMe_3)_2 \cdot 2OEt_2$ (6.4 g, 0.020 mol) and Cp_2TiCl_2 (4.8 g, 0.019 mol) were treated as in section c. After removal of $LiN(SiMe_3)_2 \cdot 0.5OEt_2$ (0.20 g, 0.00098 mol) by crystallization, the red, gummy solid obtained by solvent evaporation from the mother liquor was treated as follows. (i) A small portion was examined by ^1H NMR spectroscopy. The spectrum consisted to two broad resonances at ca. δ 6 and 0 of approximate $w_{1/2}$ = 100 Hz. This is consistent with the presence of some paramagnetic material in a largely diamagnetic sample, as previously described.[2] (ii) The remaining red material was sublimed [120 °C (10^{-3} mm)] onto a cold-finger, the sublimation apparatus being connected to a trap containing pyridine (10 mL) at −196 °C. When the sublimation was complete [the yield of the metallacycle was 4.4 g (68%)], the trap containing the pyridine was isolated from vacuum, warmed to room temperature, and gently agitated for 30 min. The trap was opened, and the white solid was collected, washed with diethyl ether (2 × 60 mL), and dried under vacuum. The white solid (1.8 g, 0.016 mol) was shown to be pyridine hydrochloride by

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melting point analysis: mp 81–82 °C (lit.[9] mp 81 °C).

Dicyclopentadienylbis[bis(trimethylsilyl)amido]zirconium(IV). Lithium bis(trimethylsilyl)amide–bis(diethyl ether) (100 mL) was added to dicyclopentadienylzirconium dichloride[7] (2.4 g, 0.0082 mol) suspended in diethl ether (100 mL). The pale yellow suspension was stirred at room temperature for 24 h. Diethyl ether was removed under reduced pressure, and the residue was heated (60 °C) under vacuum (6 h). Trituration with pentane (2 × 100 mL) followed by filtration yielded a pale yellow solution, which was then concentrated under reduced pressure to ca. 20 mL. Cooling (−70 °C) afforded white blocks, which were identified as $LiN(SiMe_3)_2{\cdot}0.5OEt_2$ (1.3 g) by ^1H NMR spectroscopy. The mother liquor was further concentrated under reduced pressure to ca. 5 mL. Cooling (−70 °C) yielded the zirconium amide, which was collected and dried under vacuum. The amide was dissolved in cold (0 °C) pentane (10 mL). Concentration to ca. 3 mL and cooling (−70 °C) afforded the pure compound in 18% yield (0.8 g). Anal. Calcd for $C_{22}H_{46}N_2Si_4Zr$: C, 48.8; H, 8.50; N, 5.18. Found: C, 48.5; H, 8.77; N, 5.02. The ^1H NMR spectrum consisted of singlets at δ 6.11, 0.53, and 0.30 due to Cp_2Zr and $[(Me_3Si)_2N]_2Zr$, in area ratio 10:18:18, respectively. The ^{13}C NMR spectrum consisted of a doublet centered at δ 115.2 (J_{CH} = 174 Hz) due to Cp_2Zr and a pair of quartest centered at δ 7.3 (J_{CH} = 117 Hz) and 6.7 (J_{CH} = 117 Hz) due to $[(Me_3Si)_2N]_2Zr$.

Preparation of $Cp_2ZrCH_2SiMe_2NSiMe_3$. Lithium bis(trimethylsilyl)amide–bis(diethyl ether) (2.3 g, 0.0075 mol) in diethyl ether (100 mL) was added to a suspension of dicyclopentadienylzirconium hydrochloride[10] (1.9 g, 0.0074 mol) in diethyl ether (50 mL). The mixture was stirred at room temperature (24 h) in the dark and then filtered. Diethyl ether was evaporated from the filtrate, and the yellow powder was extracted with pentane (2 × 50 mL). The extract was filtered, and the filtrate was concentrated under reduced pressure to ca. 10 mL and cooled (−70 °C). The white blocks were collected and shown to be $LiN(SiMe_3)_2{\cdot}OEt_2$ by ^1H NMR spectroscopy (0.70 g). The mother liquor was concentrated to ca. 3 mL and cooled (−70 °C) to yield the waxy, pale yellow metallacycle. The metallacycle sublimed [70–80 °C (10^{-3} mm)] as pale yellow sheets (0.5 g, 18%). Anal. Calcd for $C_{16}H_{27}NSi_2Zr$: C, 49.2; H, 6.92; N, 3.59. Found: C, 48.5; H, 6.88; N, 3.60. The ^1H NMR spectrum consisted of singlets at δ 5.93, 1.88, 0.27, and 0.17 due to Cp_2Zr, $ZrCH_2$, $ZrCH_2SiMe_2$, and $ZrCH_2SiMe_2NSiMe_3$ in area ratio of 10:2:6:9, respectively. The ^{13}C NMR spectrum consisted of a doublet centered at δ 111.6 (J_{CH} = 171 Hz), a triplet centered at δ 42.0 (J_{CH} = 128 Hz), and a pair of quartets centered at δ 3.50 (J_{CH} = 119 Hz) and 4.60 (J_{CH} = 117 Hz) due to Cp_2Zr, $ZrCH_2$, $ZrCH_2SiMe_2$, and $ZrCH_2Si(Me)_2NSiMe_3$, respectively.

Neither metallacycle reacts with deuterium (20 atm) at room temperature in pentane.

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Registry No. $Cp_2TiCH_2SiMe_2NSiMe_3$, 52326-35-9; $Cp_2ZnCH_2SiMe_2NSiMe_3$, 78804-37-2; Cp_2TiCl_2, 1271-19-8; Cp_2ZrCl_2, 1291-32-3; $Cp_2Zn(H)(Cl)$, 37342-97-5; $LiN(SiMe_3)_2$, 4039-32-1; $LiN(SiMe_3)_2{\cdot}2OEt_2$, 78804-38-3.

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Metal Vapor Synthesis, Chemical Oxidation, and Electrochemistry of Bis(bipyridyl)cobalt(0). Preparation of Bromide, Tetracyanoethylene, and Tetracyanoquinodimethane Salts

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The first preparation of bis(2,2′-bipyridyl)cobalt $[Co(bpy)_2]$ has been carried out by metal vapor methods. Three techniques have been employed: (a) solution, (b) cocondensation, and (c) the use of toluene-solvated Co atoms. Method c was preferred. Spectral analysis of $Co(bpy)_2$ suggests that substantial Co → bpy charge transfer has taken place. Chemical oxidations with Br_2, tetracyanoquinodimethane (TCNQ), and tetracyanoethylene (TCNE) have yielded $(bpy)_2CoBr$ with the bpy ligands highly negative, $(bpy)_2Co(TCNQ)_2$ with the bpy ligands neutral and the TCNQ ligands highly negative, and (bpy)Co(TCNE) with one bpy displaced and the other neutral. It appears that the TCNE ligand bears high negative charge. Cyclic voltammetric behavior of $Co(bpy)_2$ suggests that in acetonitrile a disproportionation reaction to produce $Co(bpy)_2^-$ and $Co(bpy)_2^+{\cdot}sol$ takes place. The electrochemical redox behavior then shows similarities to that of $Co(bpy)_3^{2+}$; that is, a series of facile, reversible electron-transfer processes are observed. Overall, $(bpy)_2Co$ appears to be a useful new Co(0) intermediate.

Introduction

When the organic chemistry of nickel vs. that elucidated for cobalt is compared, a very noticeable feature is the relative abundance of Ni(0) starting complexes but the scarcity of corresponding Co(0) complexes. We have had an interest in the chemistry of Ni(0) and Co(0) complexes as compared with that of Ni and Co atoms. Recently we have developed procedures for the facile synthesis of zerovalent bipyridyl (bpy) complexes of the group 8 transition metals. Of particular interest has been the production of usable amounts of $(bpy)_2Co^0$ from a Co atom–toluene matrix. In this reaction sequence

stable on melting

"toluene-solvated Co atoms" probably exist as highly labile

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