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Publication Date

1980-07-01

8/15/80

LBL-11189
Preprint *cs*



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

Submitted to Inorganic Chemistry

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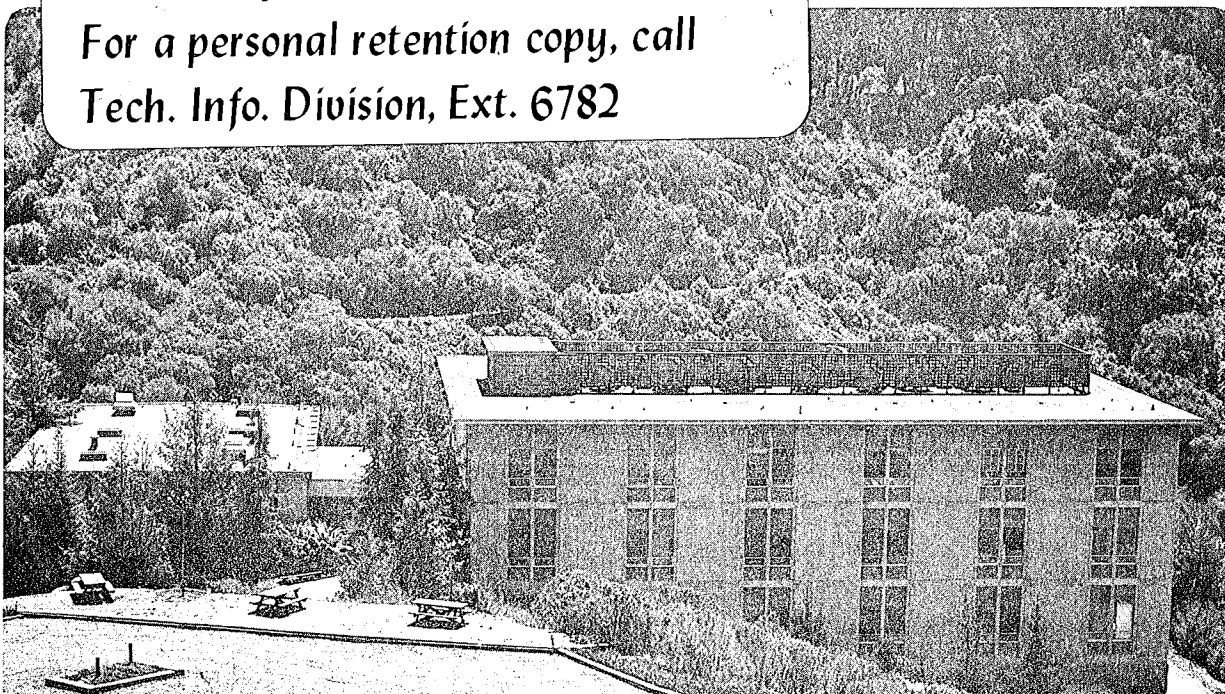
T. Don Tilley and Richard A. Andersen

July 1980

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Pentamethylcyclopentadienyl Derivatives
of the
Trivalent Lanthanide Elements
(Neodymium, Samarium, and Ytterbium)

T. Don Tilley and Richard A. Andersen*

Abstract

The anionic complexes of the type $[ML_x][(\text{Me}_5\text{C}_5)_2\text{M}'\text{Cl}_2]$, where M is lithium or sodium, L is diethyl ether or N,N,N',N'-tetramethylethylenediamine, and M' is neodymium, samarium, or ytterbium, have been prepared from the metal trichlorides and the pentamethylcyclopentadienide anion. The neutral species $(\text{Me}_5\text{C}_5)_2\text{NdCl}(\text{thf})$, $(\text{Me}_5\text{C}_5)_2\text{NdN}(\text{SiMe}_3)_2$, and $(\text{Me}_5\text{C}_5)_2\text{YbCl}(\text{thf})$ have also been prepared. The mono-ring derivatives $[\text{Na}(\text{OEt}_2)_2][(\text{C}_5\text{Me}_5)\text{NdCl}_3]$ and $(\text{Me}_5\text{C}_5)\text{Nd}[\text{N}(\text{SiMe}_3)_2]_2$ are also described.

Cyclopentadienyl derivatives of the lanthanide metals, except europium, of the type Cp_3M were first prepared by Wilkinson in 1956 from sodium cyclopentadienide and the metal trichloride in tetrahydrofuran.¹ The europium derivative, as its tetrahydrofuran complex, $\text{Cp}_3\text{Eu}(\text{thf})$, was described later.² Di- and monocyclopentadienyl compounds, Cp_2MCl and CpMCl_2 respectively, have also been prepared.^{3,4}

Tris(monomethylcyclopentadienyl)neodymium, $(\text{MeC}_5\text{H}_4)_3\text{Nd}$, is a tetramer in the solid state and it is likely that the other binary compounds are also associated into oligomeric units in the solid.⁵ The bis(cyclopentadienyl)chloro derivatives are monomeric in refluxing tetrahydrofuran but dimeric in refluxing benzene.³ A crystal structure of $(\text{MeC}_5\text{H}_4)_2\text{YbCl}$ shows that it is dimeric by way of chloride bridging groups.⁶ A σ -alkyl, Cp_2YbMe , is also dimeric in the solid state.⁷ In this case the methyl groups bridge the two ytterbium atoms. An ionic bonding model for cyclopentadienyl lanthanide derivatives has been proposed by Raymond.⁸ The organometallic chemistry of these elements has been exhaustively reviewed.⁹

A straightforward synthetic scheme for pentamethylcyclopentadiene and its alkali metal derivatives allows this useful reagent to be prepared in large quantities.¹⁰ This ligand is potentially useful for preparation of substituted derivatives as its steric size limits the degree of substitution that can be obtained. Only two pentamethylcyclopentadienyl groups can be attached to a metal atom even for large metal atoms like uranium or thorium.^{11,12}

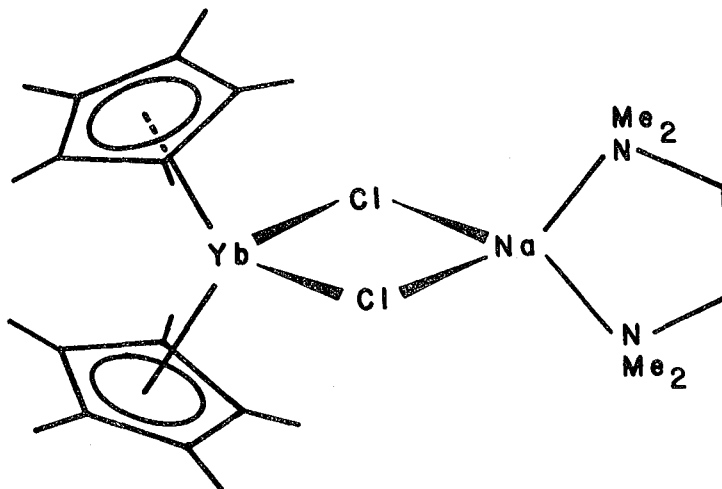
We have recently shown that europium trichloride is reduced by sodium pentamethylcyclopentadienide in refluxing tetrahydrofuran to give $(\text{Me}_5\text{C}_5)_2\text{Eu}(\text{thf})$.¹³ As a result of this observation we have investigated the reaction of the pentamethylcyclopentadienide anion with some other lanthanide trichlorides.

Ytterbium trichloride reacts with two molar equivalents of LiMe_5C_5 in tetrahydrofuran to give violet $[\text{Li}(\text{OEt}_2)_2][(\text{Me}_5\text{C}_5)_2\text{YbCl}_2]$ upon crystallization from diethyl ether. The complex is paramagnetic and the proton nuclear magnetic resonance spectrum is uninformative, as only a broad resonance was observed for the methyl group protons, a phenomenon observed for all the compounds described in this paper. Thus, at least one derivative of each compound was prepared in order to further substantiate the stoichiometry. The diethyl ether in $[\text{Li}(\text{OEt}_2)_2][(\text{Me}_5\text{C}_5)_2\text{YbCl}_2]$ can be replaced by *N,N,N',N'*-tetramethylethylenediamine giving $[\text{Li}(\text{tmed})][(\text{Me}_5\text{C}_5)_2\text{YbCl}_2]$. Anionic complexes of samarium and neodymium, $[\text{Li}(\text{tmed})][(\text{Me}_5\text{C}_5)_2\text{SmCl}_2]$, $[\text{Li}(\text{OEt}_2)][(\text{Me}_5\text{C}_5)_2\text{NdCl}_2]$ and $[\text{Li}(\text{tmed})_2][(\text{Me}_5\text{C}_5)_2\text{NdCl}_2]$ were prepared similarly.

In contrast to europium trichloride, ytterbium trichloride is not reduced by reaction of two molar equivalents of NaMe_5C_5 in tetrahydrofuran. Instead, two ytterbium(III) products are obtained when diethyl ether is used as a crystallization solvent. The first crop of crystals was $[\text{Na}(\text{OEt}_2)_2][(\text{Me}_5\text{C}_5)_2\text{YbCl}_2]$, isolated in 33% yield from a large volume of diethyl ether. The second crop of crystals from the mother liquor was the neutral complex, $(\text{Me}_5\text{C}_5)_2\text{YbCl}(\text{thf})$, isolated in 42% yield. When toluene is used

as crystallization solvent the neutral species is isolated as the only product. The anionic complex follows Curie-Weiss behavior from 4-45K, the magnetic moment being 3.91 B.M. ($\theta = -3.7\text{K}$ and $C = 1.90$). The magnetic moment of $(\text{Me}_5\text{C}_5)_2\text{YbCl}(\text{thf})$ at 28°C (Evans' method) is 4.20 B.M.

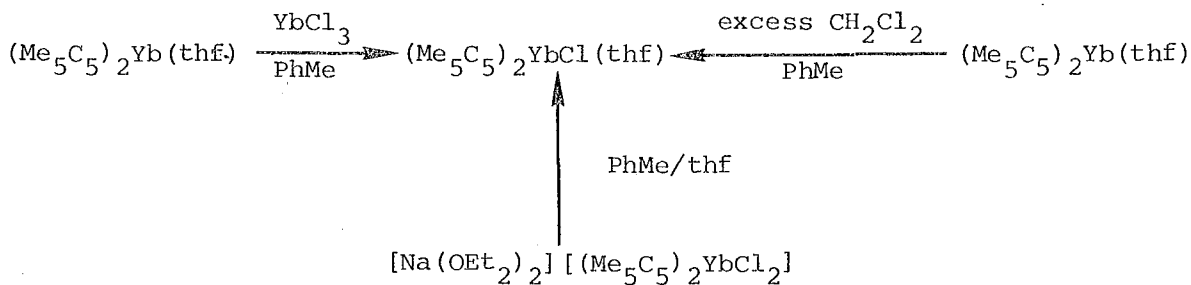
Diethyl ether in the anionic complex can be replaced by N,N',N'-tetramethylethylenediamine, yielding $[\text{Na}(\text{tmed})][(\text{Me}_5\text{C}_5)_2\text{YbCl}_2]$. Data for a crystal structure determination were collected on crystals of this complex, but unfortunately it could not be refined properly.¹⁴ A disorder in the hydrocarbon ligands allowed only the heavy atoms (Yb, Cl, and Na) to be located. The location of these atoms leaves no doubt that the gross structure is I.



A crystal structure of the related diethyl ether complex, $[\text{Li}(\text{OEt}_2)_2][(\text{Me}_5\text{C}_5)_2]$, has been determined and it has structure I, lithium replacing sodium and two diethyl ether molecules replacing a tmed group.¹⁵

The other product in the reaction of two molar equivalents of NaMe_5C_5 and YbCl_3 , $(\text{Me}_5\text{C}_5)_2\text{YbCl}(\text{thf})$, was unsuitable for a single-crystal X-ray analysis due to twinning.¹⁴ Replacement of the coordinated tetrahydrofuran by pyridine yields $(\text{Me}_5\text{C}_5)_2\text{YbCl}(\text{py})$, which also appears to be disordered.¹⁴

The neutral tetrahydrofuran complex, $(\text{Me}_5\text{C}_5)_2\text{YbCl}(\text{thf})$, can also be prepared by stirring the divalent species, $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{thf})$,¹³ with either ytterbium trichloride or dichloromethane in toluene. Further, the anionic species, $[\text{Na}(\text{OEt}_2)_2][(\text{Me}_5\text{C}_5)_2\text{YbCl}_2]$, can be converted quantitatively to the neutral trivalent, tetrahydrofuran complex by stirring in toluene with a small amount of tetrahydrofuran present.



This observation leads us to suggest that the initial product in the reaction of NaMe_5C_5 and YbCl_3 is the anionic salt, $[\text{Na}(\text{thf})_2][(\text{Me}_5\text{C}_5)_2\text{YbCl}_2]$, which in solvents less polar than tetrahydrofuran eliminates sodium chloride. The analogous lithium salts appear to be much more stable with respect to loss of LiCl , since they do not undergo this disproportionation in toluene.

The reaction between neodymium trichloride and two molar equivalents of NaMe_5C_5 in tetrahydrofuran also yields two products

on crystallization from diethyl ether, the anionic species $[\text{Na}(\text{OEt}_2)][(\text{Me}_5\text{C}_5)_2\text{NdCl}_2]$ and the neutral one, $(\text{Me}_5\text{C}_5)_2\text{NdCl}(\text{thf})$. The only product isolated from samarium trichloride and NaMe_5C_5 under similar conditions was $[\text{Na}(\text{OEt}_2)][(\text{Me}_5\text{C}_5)_2\text{SmCl}_2]$. A tmed complex of the latter can also be prepared, $[\text{Na}(\text{tmed})][(\text{Me}_5\text{C}_5)_2\text{SmCl}_2]$. Interestingly, neither the neodymium nor samarium anionic complexes eliminated sodium chloride on stirring in toluene in the presence of tetrahydrofuran.

The mono-ring complex, $[\text{Na}(\text{OEt}_2)_2][(\text{Me}_5\text{C}_5)\text{NdCl}_3]$, can be isolated from one molar equivalent of NaMe_5C_5 and neodymium trichloride in tetrahydrofuran after crystallization from diethyl ether.

It is noteworthy that complexes of the type $[\text{ML}_x][(\text{Me}_5\text{C}_5)_2\text{M}'\text{Cl}_2]$, which differ in formula only by the type of lanthanide metal M' , have superimposable infrared spectra. Further, the neutral species $(\text{Me}_5\text{C}_5)_2\text{MCl}(\text{thf})$, where M is Nd or Yb , also have superimposable infrared spectra. The infrared absorptions are listed in the experimental section.

The anionic complexes are useful synthetic reagents for the preparation of pentamethylcyclopentadienyl derivatives. The silylamides $(\text{Me}_5\text{C}_5)_2\text{NdN}(\text{SiMe}_3)_2$ and $(\text{Me}_5\text{C}_5)\text{Nd}[\text{N}(\text{SiMe}_3)_2]_2$ have been obtained from reaction of $[\text{Li}(\text{OEt}_2)_2][(\text{Me}_5\text{C}_5)_2\text{NdCl}_2]$ and $[\text{Na}(\text{OEt}_2)_2][(\text{Me}_5\text{C}_5)\text{NdCl}_3]$ with sodium bis(trimethylsilyl)amide in toluene, respectively. The mono-silylamide, $(\text{Me}_5\text{C}_5)_2\text{NdN}(\text{SiMe}_3)_2$, has an infrared spectrum identical to the related uranium(III) derivative, $(\text{Me}_5\text{C}_5)_2\text{UN}(\text{SiMe}_3)_2$.¹⁶

Experimental

Microanalyses were performed by the microanalytical laboratory of this department. Infrared spectra were recorded on a Perkin-Elmer 597 machine as Nujol mulls between cesium iodide windows. The solid state magnetic susceptibility measurements were performed as previously described.¹⁷ Solution susceptibility measurements were determined by Evans' method.¹⁸ All operations were carried out under nitrogen.

Sodium Pentamethylcyclopentadienyltrichlorobis(diethyl ether)-neodymate(III). Sodium pentamethylcyclopentadienide (3.4 g, 0.021 mol) in tetrahydrofuran (50 mL) was added to neodymium trichloride (5.4 g, 0.021 mol) in tetrahydrofuran (75 mL) and the mixture was refluxed for 12 h. The blue-green solution was evaporated to dryness and the residue was extracted with diethyl ether (2 x 100 mL). The combined extracts were concentrated to ca. 80 mL and cooled to -10°C. The light blue prisms were collected and dried under vacuum. Yield was 7.4 g (62%).
I.r. 2720w, 1296w br, 1181w, 1150w, 1090s, 1063s, 1018w sh, 1007m, 968w, 911w, 862m, 833w sh, 799w, 791w, 721m, 588w, and 392m cm^{-1} .

Lithium Bis(pentamethylcyclopentadienyl)dichlorobis(diethyl ether)neodymate(III). Lithium pentamethylcyclopentadienide (4.0 g, 0.028 mol) was added to neodymium trichloride (3.5 g, 0.014 mol) and tetrahydrofuran (150 mL) was added. The suspension was refluxed for 12 h. The tetrahydrofuran was removed in vacuum and the residue was extracted with diethyl ether (2 x 100 mL). The red extracts were combined, concentrated to ca. 100 mL,

and cooled (-10°C). The large blue prisms (6.0 g, 66%) were collected and dried under vacuum. I.r. 2728w, 2184w, 1949w, 1299m, 1182s, 1154m, 1089s br, 1059s br, 1018s br, 909m, 834m, 790s, 722w, 632w, 619w, 592w, 552w, 503m, 384s br, 304s br cm^{-1} .

Lithium Bis(pentamethylcyclopentadienyl)dichlorobis(N,N,N',-N'-tetramethylethylenediamine)neodymate(III). N,N,N',N'-Tetramethylethylenediamine (0.3 mL, ca. 2 mmol) was added to $[\text{Li}(\text{OEt})_2]_2$ - $[(\text{Me}_5\text{C}_5)_2\text{NdCl}_2]$ (0.58 g, 0.00091 mol) in diethyl ether (30 mL). After stirring for 3 h, the volatile material was removed in vacuum. The residue was extracted with diethyl ether (30 mL), concentrated to ca. 20 mL and cooled (-10°C). The light blue needles (0.38 g, 58%) were collected and dried in vacuum. I.r. 2720w, 1369m, 1290s, 1249m, 1188m, 1163s, 1131s, 1100m, 1070m, 1034s, 1017s, 948s, 789s, 776w, 722w, 593m, 496m br, 446m, 378m sh, 342m, 300s br, 229s br cm^{-1} .

Sodium Bis(pentamethylcyclopentadienyl)dichloro(diethyl ether)neodymate(III). Addition of sodium pentamethylcyclopentadienide (4.5 g, 0.029 mol) in tetrahydrofuran (75 mL) to neodymium trichloride (3.6 g, 0.014 mol) suspended in tetrahydrofuran (25 mL) resulted in a green solution. After refluxing for 8 h, the tetrahydrofuran was removed under vacuum and the residue was extracted with diethyl ether (2 x 100 mL). The green extracts were concentrated to ca. 150 mL and cooled (-10°C). The light blue prisms (4.0 g, 48%) were collected and dried under vacuum. I.r. 2722w, 2180w, 1943w, 1306w, 1186m, 1157m, 1123s, 1098s, 1069s, 1021s, 913w, 841w, 802w, 796w sh, 722w, 628w, 618w, 594w, 379m br, 312s br cm^{-1} .

Bis(pentamethylcyclopentadienyl)chloroneodymium(III)
tetrahydrofuran. The mother liquor from the above reaction was concentrated to ca. 20 mL. Cooling (-10°C) yielded green prisms (1.7 g, 23%). I.r. 2721w, 1948w, 1343w, 1298w, 1262w, 1248w, 1179m, 1151w, 1122s, 1076w, 1019s, 953w, 917m, 863s, 845w sh, 802w, 723w, 681m, 628w, 617w, 593m, 551w, 382s br, 309s br, 243m cm^{-1} .

Lithium Bis(pentamethylcyclopentadienyl)dichloro(N,N,N',N'-tetramethylethylenediamine)samarate(III). Lithium pentamethylcyclopentadienide (2.1 g, 0.015 mol) was added to samarium trichloride (1.9 g, 0.0076 mol) and tetrahydrofuran was added (60 mL). After refluxing for 8 h, the suspension was evaporated to dryness. The residue was extracted with toluene (50 mL) and evaporated to dryness. Tetrahydrofuran (10 mL) and N,N,N',N'-tetramethylethylenediamine (1.5 mL, ca. 10 mmol) were added to the residue. After stirring the orange solution for 2 h, the volatile material was removed under vacuum. The residue was washed with pentane (20 mL), then crystallized from tetrahydrofuran (10 mL, -10°C) as yellow prisms in 33% (1.5 g) yield.

Sodium Bis(pentamethylcyclopentadienyl)dichloro(diethyl ether)samarate(III). Sodium pentamethylcyclopentadienide (2.2 g, 0.014 mol) in tetrahydrofuran (75 mL) was added to samarium trichloride (1.8 g, 0.0069 mol) in tetrahydrofuran (25 mL). The brown suspension was stirred for 24 h, then evaporated to dryness in vacuum. The residue was extracted with diethyl ether (2 x 75 mL) and the combined, orange extracts were concentrated to ca. 70 mL and cooled (-10°C). The large, orange prisms were

collected and dried in vacuum. The yield was 36% (2.9 g).

Sodium Bis(pentamethylcyclopentadienyl)dichloro(N,N,N',N'-tetramethylethylenediamine)samarate(III). N,N,N',N'-Tetramethylethylenediamine (0.3 mL, ca. 2 mmol) was added to [Na(OEt₂)] [(Me₅C₅)₂SmCl₂] (0.80 g, 0.0014 mol) in diethyl ether (15 mL). The yellow precipitate was stirred for 1 h, then crystallized from tetrahydrofuran as yellow needles in 65% (0.56 g) yield.

Lithium Bis(pentamethylcyclopentadienyl)dichlorobis(diethyl ether)ytterbate(III). Lithium pentamethylcyclopentadienide (2.7 g, 0.019 mol) and ytterbium trichloride (2.6 g, 0.0094 mol) were mixed and tetrahydrofuran (75 mL) was added. The mixture was stirred for one week. Tetrahydrofuran was removed under vacuum and the residue was extracted with diethyl ether (2 x 60 mL). The violet extracts were concentrated to ca. 30 mL and cooled (-10°C) to give violet needles (4.5 g, 72%).

Lithium Bis(pentamethylcyclopentadienyl)dichloro(N,N,N',N'-tetramethylethylenediamine)ytterbate(III). N,N,N',N'-Tetramethylethylenediamine (0.3 mL, ca. 2 mmol) was added to [Li(OEt₂)₂] [(Me₅C₅)₂YbCl₂] (0.60 g, 0.90 mmol) in diethyl ether (40 mL). The violet solution was stirred for 5 h and the volatile material was removed in vacuum. The residue was crystallized from diethyl ether (ca. 20 mL., -10°C) as violet needles in 53% (0.30 g) yield.

Sodium Bis(pentamethylcyclopentadienyl)dichlorobis(diethyl ether)ytterbate(III). Sodium pentamethylcyclopentadienide (3.8 g, 0.024 mol) in tetrahydrofuran (75 mL) was added to ytterbium trichloride (3.3 g, 0.012 mol) suspended in tetrahydrofuran (25 mL).

The suspension was stirred for 15 h. The tetrahydrofuran was evaporated under vacuum and the residue was extracted with diethyl ether (2 x 100 mL). The purple extracts were concentrated to ca. 100 mL and cooled (-10°C). The violet prisms were collected and dried in vacuum, yield was 2.7 g (33%). I.r. 2723w, 1307w, 1290w, 1187w sh, 1172w sh, 1152m, 1124m, 1084s br, 1046w, 1024m, 931m, 845m, 824w, 804w, 723w, 598m, 444w, 390m br, 309s br cm^{-1} .

Bis(pentamethylcyclopentadienyl)chloroytterbium(III)

tetrahydrofuran. (a). From Mother Liquor (above). The mother liquor from the preceding recipe was concentrated to ca. 30 mL and cooled (-10°C). The violet needles were collected and dried under vacuum. Yield was 42% (2.8 g). The mass spectrum contained a $(\text{M-thf})^{+}$ peak at 479; $(\text{Me}_5\text{C}_5)_2^{174}\text{Yb}^{35}\text{Cl}$ requires 479.

(b). By Crystallization from Toluene. Sodium pentamethylcyclopentadienide (4.7 g, 0.030 mol) in tetrahydrofuran (75 mL) was added to a cold (-70°C) suspension of ytterbium trichloride (4.2 g, 0.015 mol) in tetrahydrofuran (50 mL). The blue suspension turned to red as the solution was allowed to warm to room temperature. The red suspension was stirred for 15 h. Tetrahydrofuran was removed under vacuum and the residue was extracted with toluene (2 x 100 mL). The extracts were combined, concentrated to ca. 70 mL and cooled (-10°C). The violet needles were collected, dried in vacuum, and were identified by mp and ir. Yield was 5.2 g (63%). (c). From $[\text{Na}(\text{OEt}_2)_2][(\text{Me}_5\text{C}_5)_2\text{YbCl}_2]$. The anionic complex

(0.65 g, 0.0095 mol) was suspended in toluene (40 mL) and tetrahydrofuran (0.5 mL) was added, yielding a purple solution which was stirred for 8 h. The volatile material was removed under vacuum and the residue was crystallized from toluene (ca. 10 mL, -10°C). The mp and ir were identical to those of an authentic specimen. (d). From Dichloromethane. Dichloromethane (0.50 mL, 7.8 mmol) was added to a toluene solution (20 mL) of $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{thf}) \cdot 1/2(\text{PhMe})$ (0.66 g, 0.0012 mol) cooled to 0°C . After stirring at 0°C for 30 min the volatile material was evaporated and the residue crystallized from toluene (ca. 8 mL, -10°C), in 70% (0.45 g) yield. The mp and ir were identical to those of the authentic specimen. (e). From Ytterbium Trichloride. The $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{thf}) \cdot 1/2(\text{PhMe})$ (0.52 g, 0.00093 mol), dissolved in toluene (30 mL), was added to a suspension of ytterbium trichloride (0.26 g, 0.00093 mol) in toluene (15 mL). After stirring for 12 h the solution was filtered, concentrated to ca. 10 mL and cooled (-10°C). The violet crystals (0.30 g, 59%) were identified by their mp and ir.

Bis(pentamethylcyclopentadienyl)chloroytterbium(III)pyridine. Pyridine (1 mL, an excess) was added to $(\text{Me}_5\text{C}_5)_2\text{YbCl}(\text{thf})$ (0.84 g, 0.0015 mol) dissolved in diethyl ether (10 mL). After stirring for 2 h the volatile material was removed in vacuum and the residue was crystallized from diethyl ether (ca. 20 mL, -10°C) as purple prisms in 47% (0.40 g) yield. I.r. 3048w, 2720w, 1947w, 1640m,

1600s, 1570w, 1233w, 1215m, 1153w, 1062m, 1039w, 1019w sh, 1009m, 959w, 800w, 756s, 707s; 627m, 592w, 433m, 389m, 310s br cm^{-1} .

Sodium Bis(pentamethylcyclopentadienyl)dichloro(N,N,N',N'-tetramethylethylenediamine)ytterbate(III). N,N,N',N'-Tetramethylethylenediamine (0.3 mL, 2 mmol) was added to a solution of $[\text{Na}(\text{OEt}_2)_2][(\text{Me}_5\text{C}_5)_2\text{YbCl}_2]$ (0.83 g, 0.0012 mol) in diethyl ether (30 mL). The mixture was stirred for 1 h, and the volatile material was evaporated under vacuum. The residue was extracted with diethyl ether (2 x 50 mL), and the combined extracts were concentrated to ca. 40 mL. Cooling (-10°C) yielded violet prisms in 41% (0.32 g) yield.

Bis(pentamethylcyclopentadienyl)[bis(trimethylsilyl)amido]-neodymium(III). Sodium bis(trimethylsilyl)amide (0.16 g, 0.00087 mol) in toluene (25 mL) was added to a toluene (20 mL) solution of $[\text{Li}(\text{OEt}_2)_2][(\text{Me}_5\text{C}_5)_2\text{NdCl}_2]$ (0.55 g, 0.00086 mol). The mixture was stirred for 8 h, toluene was removed under vacuum, and the residue extracted with pentane (2 x 20 mL). The extracts were combined, concentrated to ca. 13 mL and cooled (-10°C). The large, blue needles were collected and dried in vacuum, yield was 0.25 g (51%). I.r. 2722w, 1257w sh, 1242s, 1032s br, 863s br, 762s br, 669m, 592s, 382w sh, 370s, 290s br cm^{-1} .

Pentamethylcyclopentadienylbis[bis(trimethylsilyl)amido]-neodymium(III). Sodium bis(trimethylsilyl)amide (0.72 g, 0.0039 mol) in toluene (50 mL) was added to $[\text{Na}(\text{OEt}_2)_2][(\text{Me}_5\text{C}_5)\text{NdCl}_3]$ (1.1 g, 0.0019 mol) in toluene (10mL). The mixture was stirred for 12 h,

then evaporated to dryness. The residue was extracted with pentane (50 mL), and the extract was concentrated to ca. 10 mL. Cooling (-10°C) yielded blue prisms in 72% (0.84 g) yield. I.r. 1246s br, 990s br, 878s sh, 830s br, 763s, 752w sh, 723m, 670s, 660w sh, 598s, 371s, 306s cm^{-1} .

Acknowledgement

This work was supported by the Division of Nuclear Sciences, Office of Basic Energy Sciences, U.S. Department of Energy. We thank Dr. P.L. Watson for communicating her results to us in advance of publication.

Table

Some Physical Properties of the Pentamethylcyclopentadienyl Derivatives

Compound	Melting Point (°C)	Color	Analysis (%)					
			Calculated			Found		
			C	H	N	C	H	N
[Na(OEt ₂) ₂][(Me ₅ C ₅)NdCl ₃]	125 dec	blue	38.3	6.33		38.6	5.69	
[Li(OEt ₂) ₂][(Me ₅ C ₅) ₂ NdCl ₂]	114 dec	blue	52.5	7.87		52.2	7.78	
[Li(tmed) ₂][(Me ₅ C ₅) ₂ NdCl ₂]	>300	blue	53.0	8.62	7.73	53.3	8.47	7.69
[Na(OEt ₂)][(Me ₅ C ₅) ₂ NdCl ₂]	>300	blue	49.5	6.92		50.1	6.66	
[Li(tmed)][(Me ₅ C ₅) ₂ SmCl ₂]	200 dec	yellow	50.8	7.54	4.56	50.5	7.71	4.40
[Na(OEt ₂)][(Me ₅ C ₅) ₂ SmCl ₂]	>300	orange	49.0	6.85		48.5	6.49	
[Na(tmed)][(Me ₅ C ₅) ₂ SmCl ₂]	>300	yellow	49.5	7.35	4.44	49.7	7.36	3.20
[Li(OEt ₂) ₂][(Me ₅ C ₅) ₂ YbCl ₂]	130 dec	violet	50.2	7.53	10.6(a)	50.5	7.59	9.38(a)
[Li(tmed)][(Me ₅ C ₅) ₂ YbCl ₂]	255 dec	violet	49.0	7.27	4.39	50.0	7.43	4.50
[Na(OEt ₂) ₂][(Me ₅ C ₅) ₂ YbCl ₂]	280 dec	violet	49.1	7.36	10.4(a)	49.0	7.16	9.00(a)
[Na(tmed)][(Me ₅ C ₅) ₂ YbCl ₂]	120 dec	violet	47.8	7.09	4.28	46.3	7.05	3.10
(Me ₅ C ₅) ₂ YbCl(thf)	221-223	violet	52.4	6.96	6.44(a)	52.6	7.05	6.04(a)
(Me ₅ C ₅) ₂ YbCl(py)	270-272	purple	53.8	6.32	2.51	54.4	6.37	2.53
					6.35(a)			5.96(a)
(Me ₅ C ₅) ₂ NdN(SiMe ₃) ₂	>300	blue	54.3	8.41	2.44	53.3	8.28	2.36
(Me ₅ C ₅)Nd[N(SiMe ₃) ₂] ₂	234-236	blue	44.0	8.56	4.67	42.0	8.46	4.30
(Me ₅ C ₅) ₂ NdCl(thf)	220-223	green	55.2	7.33		55.4	7.28	

(a) Chloride

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This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.