M = Ni, R = Me, 78064-10-5; **4**, M = Fe, R = Me, 78065-22-2; **4**, Me = Cu, R = Me, 78090-06-9; **4**, M = Ni, R = *sec*-butyl, 66114-34-9; **4**, M = Cu, R = *sec*-butyl, 78065-23-3; Mn(4′-MeL)OAc, 78065-24-4; Fe(4′-MeL)OAc, 78065-25-5; Co(4′-MeL)OAc, 78065-26-6; Ni(4′-HMeL)OAc, 78065-27-7; Cu(4′-MeL)OAc, 78065-28-8; Fe(4′-MeLH)Br_2, 78065-29-9; Mn(4′-MeL)$_2$, 78065-30-2; Fe(4′-MeL)$_2$, 78065-31-3; Co(4′-MeL)$_2$, 78065-32-4; Ni(4′-MeL)$_2$, 78065-33-5; Zn(4′-MeL)$_2$, 78065-34-6; CoL_2, 14911-23-0; Co(5′-NO_2L)$_2$, 78090-07-0; Co(5′-ClL)$_2$, 78090-08-1; Cu(4′-*sec*-BuL)$_2$, 78065-35-7; Co(4′-MeL)(5′-ClL), 78065-36-8; Co(4′-MeL)$_2$$PF_6$, 78065-38-0; Co(4′-MeL)$_2$($Ph_4$B), 78065-39-1; [(4′-MeL)CoL-LCo-(4′-MeL)]PF_6, 78355-31-4; [(4′-MeL)CoL-LCo(4′-MeL)](ClO_4)$_2$, 78090-10-5; 2-aminopyridine, 504-29-0; 2-amino-4-methylpyridine, 695-34-1; 2-amino-5-methylpyridine, 1603-41-4; 2-amino-3,5-dimethylpyridine, 41995-30-6; 2-amino-4-ethylpyridine, 33252-32-3; 2-amino-4-*n*-propylpyridine, 61702-15-6; 2-amino-4-*sec*-butylpyridine, 61702-16-7; 2-amino-4-*tert*-butylpyridine, 33252-26-5; 2-amino-4-*n*-amylpyridine, 60781-86-4; 1,2,4,5-tetracyanobenzene, 712-74-3.

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

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The anionic complexes of the type $[ML_x][(Me_5C_5)_2M'Cl_2]$, 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 $(Me_5C_5)_2NdCl(THF)$, $(Me_5C_5)_2NdN(SiMe_3)_2$, and $(Me_5C_5)_2YbCl(THF)$ have also been prepared. The mono-ring derivatives $[Na(OEt_2)_2][(C_5Me_5)NdCl_3]$ and $(Me_5C_5)Nd[N(SiMe_3)_2]_2$ 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, $Cp_3Eu(THF)$, was described later.[2] Di- and monocyclopentadienyl compounds, Cp_2MCl and $CpMCl_2$, respectively, have also been prepared.[3,4]

Tris(methylcyclopentadienyl)neodymium, $(MeC_5H_4)_3Nd$, 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 $[(MeC_5H_4)_2YbCl]_2$ shows that it is dimeric by way of chloride bridging groups.[6] A σ-alkyl, $[Cp_2YbMe]_2$, is also dimeric in the solid state.[7] In this case the methyl groups bridge the two ytterbium atoms. An ionic bonding model for cyclopentadienyllanthanide 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 such as uranium or thorium.[11,12]

We have recently shown that europium trichloride is reduced by sodium pentamethylcyclopentadienide in refluxing tetrahydrofuran to give $(Me_5C_5)_2Eu(THF)$.[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 2 molar equiv of $LiMe_5C_5$ in tetrahydrofuran to give violet $[Li(OEt_2)_2][(Me_5C_5)_2YbCl_2]$ upon crystallization from diethyl ether. Some physical properties are shown in Table I. 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 $[Li(OEt_2)_2][(Me_5C_5)_2YbCl_2]$ can be replaced by *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, giving $[Li(tmed)][(Me_5C_5)_2YbCl_2]$. Anionic complexes of samarium and neodymium, $[Li(tmed)][(Me_5C_5)_2SmCl_2]$, $[Li(OEt_2)_2][(Me_5C_5)_2NdCl_2]$, and $[Li(tmed)_2][(Me_5C_5)_2NdCl_2]$, were prepared similarly. It is rather curious that the neodymium compound yields a 2:1 tmed complex whereas the samarium compound yields a 1:1 tmed complex. Another way of saying this is that the former is more thermodynamically stable than the latter (four Li–N bonds rather than two Li–N and two Li–Cl bonds and the associated changes in the relative lattice energies). In absence of thermochemical data we cannot account for this behavior in a reasonable manner.

In contrast to europium trichloride, ytterbium trichloride is not reduced by reaction of 2 molar equiv of $NaMe_5C_5$ in tetrahydrofuran. Instead, two ytterbium(III) products are obtained when diethyl ether is used as a crystallization solvent.

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(1) Birmingham, J. M.; Wilkinson, G. *J. Am. Chem. Soc.* **1956**, *78*, 42.
(2) Manastyrskyj, S.; Dubeck, M. *Inorg. Chem.* **1964**, *3*, 1647.
(3) Maginn, R. E.; Manastyrskyj, S.; Dubeck, M. *J. Am. Chem. Soc.* **1963**, *85*, 672.
(4) Manastyrskyj, S.; Maginn, R. E.; Dubeck, M. *Inorg. Chem.* **1963**, *2*, 904.
(5) Burns, J. H.; Baldwin, W. H.; Fink, F. H. *Inorg. Chem.* **1974**, *13*, 1916.
(6) Baker, E. C.; Brown, L. D.; Raymond, K. N. *Inorg. Chem.* **1975**, *14*, 1376.
(7) Holton, J.; Lappert, M. F.; Scollary, G. R.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45.
(8) Baker, E. C.; Halstead, G. W.; Raymond, K. N. *Struct. Bonding (Berlin)* **1976**, *25*, 23. Raymond, K. N.; Eigenbrot, C. W. *Acc. Chem. Res.* **1980**, *13*, 273. We thank Professor Raymond for a copy of this review in advance of publication.
(9) Marks, T. J. *Prog. Inorg. Chem.* **1978**, *24*, 51.
(10) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1.
(11) Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3939.
(12) Green, J. C.; Watt, O. *J. Organomet. Chem.* **1978**, *153*, C40.
(13) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Ruben, H.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1980**, *19*, 2999.

0020-1669/81/1320-3267$01.25/0

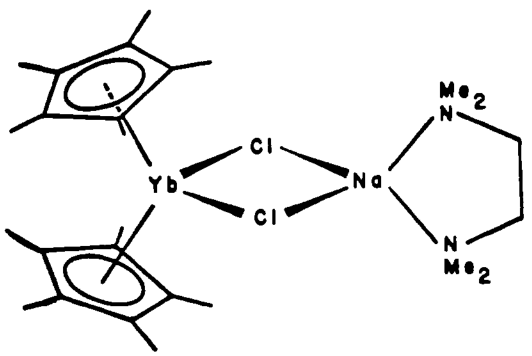
Table I. Some Physical Properties of the Pentamethylcyclopentadienyl Derivatives

compd	mp, °C	color	anal. calcd, %			anal. found, %		
			C	H	N	C	H	N
$[Na(OEt_2)_2][(Me_5C_5)NdCl_3]$	125 dec	blue	38.3	6.33		38.6	5.69	
$[Li(OEt_2)_2][(Me_5C_5)_2NdCl_2]$	114 dec	blue	52.5	7.87		52.2	7.78	
$[Li(tmed)_2][(Me_5C_5)_2NdCl_2]$	>300	blue	53.0	8.62	7.73	53.3	8.47	7.69
$[Na(OEt_2)][(Me_5C_5)_2NdCl_2]$	>300	blue	49.5	6.92		50.1	6.66	
$[Li(tmed)][(Me_5C_5)_2SmCl_2]$	200 dec	yellow	50.8	7.54	4.56	50.5	7.71	4.40
$[Na(OEt_2)][(Me_5C_5)_2SmCl_2]$	>300	orange	49.0	6.85		48.5	6.49	
$[Na(tmed)][(Me_5C_5)_2SmCl_2]$	>300	yellow	49.5	7.35	4.44	49.7	7.36	3.20
$[Li(OEt_2)_2][(Me_5C_5)_2YbCl_2]$	130 dec	violet	50.2	7.53	10.6[a]	50.5	7.59	9.38[a]
$[Li(tmed)][(Me_5C_5)_2YbCl_2]$	255 dec	violet	49.0	7.27	4.39	50.0	7.43	4.50
$[Na(OEt_2)_2][(Me_5C_5)_2YbCl_2]$	280 dec	violet	49.1	7.36	10.4[a]	49.0	7.16	9.00[a]
$[Na(tmed)][(Me_5C_5)_2YbCl_2]$	120 dec	violet	47.8	7.09	4.28	46.3	7.05	3.10
$(Me_5C_5)_2YbCl(THF)$	221–223	violet	52.4	6.96	6.44[a]	52.6	7.05	6.04[a]
$(Me_5C_5)_2YbCl(py)$	270–272	purple	53.8	6.32	2.51 6.35[a]	54.4	6.37	2.53 5.96[a]
$(Me_5C_5)_2NdN(SiMe_3)_2$	>300	blue	54.3	8.41	2.44	53.3	8.28	2.36
$(Me_5C_5)Nd[N(SiMe_3)_2]_2$	234–236	blue	44.0	8.56	4.67	42.0	8.46	4.30
$(Me_5C_5)_2NdCl(THF)$	220–223	green	55.2	7.33		55.4	7.28	
$(Me_5C_5)_2YbN(SiMe_3)_2$	294–295	purple	51.7	8.01	2.32	50.9	7.82	2.18

[a] Chloride.

The first crop of crystals was $[Na(OEt_2)_2][(Me_5C_5)_2YbCl_2]$, isolated in 33% yield from a large volume of diethyl ether. The second crop of crystals from the mother liquor was the neutral complex $(Me_5C_5)_2YbCl(THF)$, isolated in 42% yield. The coordinated tetrahydrofuran in this molecule is readily identified by infrared absorptions at 1014 and 862 cm^{-1} and by comparison to an authentic specimen prepared from $(Me_5C_5)_2Yb(THF)$ and $YbCl_3$ in toluene (see below). When toluene is used as the crystallization solvent, the neutral species is isolated as the only product. The anionic complex follows Curie–Weiss behavior from 4 to 45 K, the magnetic moment being 3.91 μ_B ($\theta = -3.7$ K and $C = 1.90$). The magnetic moment of $(Me_5C_5)_2YbCl(THF)$ at 28 °C (Evans' method) is 4.20 μ_B.

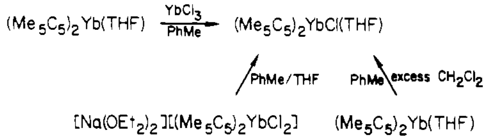
Diethyl ether in the anionic complex can be replaced by *N,N,N′,N′*-tetramethylethylenediamine, yielding $[Na(tmed)][(Me_5C_5)_2YbCl_2]$. Data for a crystal structure determination were collected on crystals of this complex, but unfortunately it could not be refined properly.[14] A disorder in the hydrocarbon 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 $[Li(OEt_2)_2][(Me_5C_5)_2YbCl_2]$ has been determined, and it has structure I, with lithium replacing sodium and two diethyl ether molecules replacing a tmed group.[15] Chloride-bridged structures of this type have been proposed previously.[19–21]



I

The other product in the reaction of 2 molar equiv of $NaMe_5C_5$ and $YbCl_3$, $(Me_5C_5)_2YbCl(THF)$, was unsuitable for a single-crystal X-ray analysis due to twinning.[14] Replacement of the coordinated tetrahydrofuran by pyridine yields $(Me_5C_5)_2YbCl(py)$, which also appears to be disordered.[14]

The neutral tetrahydrofuran complex, $(Me_5C_5)_2YbCl(THF)$, can also be prepared by stirring the divalent species $(Me_5C_5)_2Yb(THF)$[13] with either ytterbium trichloride or dichloromethane in toluene. Further, the anionic species $[Na(OEt_2)_2][(Me_5C_5)_2YbCl_2]$ can be converted quantitatively to the neutral trivalent, tetrahydrofuran complex by stirring in toluene with a small amount of tetrahydrofuran present (eq 1). This observation leads us to suggest that the initial product in the reaction of $NaMe_5C_5$ and $YbCl_3$ is the anionic salt $[Na(THF)_2][(Me_5C_5)_2YbCl_2]$, 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.



(1)

The reaction between neodymium trichloride and 2 molar equiv of $NaMe_5C_5$ in tetrahydrofuran also yields two products on crystallization from diethyl ether: the anionic species $[Na(OEt_2)][(Me_5C_5)_2NdCl_2]$ and the neutral one $(Me_5C_5)_2NdCl(THF)$. The only product isolated from samarium trichloride and $NaMe_5C_5$ under similar conditions was $[Na(OEt_2)][(Me_5C_5)_2SmCl_2]$. A tmed complex of the latter can also be prepared; $[Na(tmed)][(Me_5C_5)_2SmCl_2]$. Interestingly, neither the neodymium nor samarium anionic complexes eliminated sodium chloride on stirring in toluene in the presence of tetrahydrofuran. However, extraction of the re-

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(14) Zalkin, A., personal communication. We thank Dr. Zalkin for his valuable help in the crystallography.

(15) Watson, P. L., personal communication.

(16) Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Vollmer, S. H.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 5075.

(17) Andersen, R. A.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1978**, *17*, 2317.

(18) Evans, D. F. *J. Chem. Soc.* **1958**, 2003.

(19) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1980**, 652.

(20) Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1980**, *19*, 2190.

(21) Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Holton, J.; McMeeking, J.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1978**, 40.

(22) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219.

Table II. Infrared Data (cm^{-1}) of the Pentamethylcyclopentadienyl Derivatives

$[Na(OEt_2)_2][(Me_5C_5)NdCl_3]$	2720 w, 1296 w, br, 1181 w, 1150 w, 1090 s, 1063 s, 1018 w sh, 1007 m, 968 w, 911 w, 862 m, 833 w sh, 799 w, 791 w, 721 w, 721 m, 588 w, 392 m
$[Li(OEt_2)_2][(Me_5C_5)_2NdCl_2]$	2728 w, 2184 w, 1949 w, 1299 m, 1182 s, 1154 m, 1089 s br, 1059 s br, 1018 s br, 909 m, 834 m, 790 s, 722 w, 632 w, 619 w, 592 w, 552 w, 503 m, 384 s br, 304 s br
$[Li(tmed)_2][(Me_5C_5)_2NdCl_2]$	2720 w, 1369 m, 1290 s, 1249 m, 1188 m, 1163 s, 1131 s, 1100 m, 1070 m, 1034 s, 1017 s, 948 s, 789 s, 776 w, 722 w, 593 m, 496 m br, 446 m, 378 m sh, 342 m, 300 s br, 229 s br
$[Na(OEt_2)][(Me_5C_5)_2NdCl_2]$	2722 w, 2180 w, 1943 w, 1306 w, 1186 m, 1157 m, 1123 s, 1098 s, 1069 s, 1021 s, 913 w, 841 w, 802 w, 796 w sh, 722 w, 628 w, 618 w, 594 w, 379 m, br, 312 s br
$[Na(OEt_2)_2][(Me_5C_5)_2YbCl_2]$	2723 w, 1307 w, 1290 w, 1187 w sh, 1172 w sh, 1152 m, 1142 m, 1084 s br, 1046 w, 1024 m, 931 m, 845 m, 824 w, 804 w, 723 w, 598 m, 444 w, 390 m, br, 309 s
$(Me_5C_5)_2NdCl(THF)$	2721 w, 1948 w, 1343 w, 1298 w, 1262 w, 1248 w, 1179 m, 1151 w, 1122 s, 1076 w, 1019 s, 953 w, 917 m, 863 s, 845 w sh, 802 w, 723 w, 681 m, 628 w, 617 w, 593 m, 551 w, 382 s br, 309 s br, 243 m
$(Me_5C_5)_2YbCl(py)$	3048 w, 2720 w, 1947 w, 1640 m, 1600 s, 1570 w, 1233 w, 1215 m, 1153 w, 1062 m, 1039 w, 1019 w sh, 1009 m, 959 w, 800 w, 756 s, 707 s, 627 m, 592 w, 433 m, 389 m, 310 s br
$(Me_5C_5)_2NdN(SiMe_3)_2$	2722 w, 1257 w sh, 1242 s, 1032 s br, 863 s br, 762 s br, 669 m, 592 s, 382 w sh, 370 s, 290 s br
$(Me_5C_5)Nd[N(SiMe_3)_2]_2$	1246 s br, 990 s br, 878 s sh, 830 s br, 763 s, 752 w sh, 723 m, 670 s, 660 w sh, 598 s, 371 s, 306 s
$(Me_5C_5)_2YbN(SiMe_3)_2$	2710 w, 1256 w sh, 1242 s, 988 s br, 868 s br, 820 s br, 777 m, 749 w, 655 m, 609 m, 383 m, 298 s

action product of neodymium trichloride and sodium pentamethylcyclopentadienide (2 molar equiv) in tetrahydrofuran with pentane yields only the green, neutral species $(Me_5C_5)_2NdCl(THF)$.

Two papers have appeared, after submission of this paper, that report some of the compounds described herein.[19,20] The latter paper refers to a green oil, suggested to contain $[(Me_5C_5)_2NdCl]_2$, present in the preparation of $[Li(THF)_2][(Me_5C_5)_2NdCl_2]$. This green material was not isolated. We suggest that it is the mononuclear tetrahydrofuran complex $(Me_5C_5)_2NdCl(THF)$.

The mono-ring complex $[Na(OEt_2)_2][(Me_5C_5)NdCl_3]$ can be isolated from 1 molar equiv of $NaMe_5C_5$ and neodymium trichloride in tetrahydrofuran after crystallization from diethyl ether.

It is noteworthy that complexes of the type $[ML_x][(Me_5C_5)_2M'Cl_2]$, which differ in formula only by the type of lanthanide metal M′, have superimposable infrared spectra. Further, the neutral species $(Me_5C_5)_2MCl(THF)$, where M is Nd or Yb, also have superimposable infrared spectra. The infrared absorptions are listed in Table II.

The anionic complexes are useful synthetic reagents for the preparation of pentamethylcyclopentadienyl derivatives. The silylamides $(Me_5C_5)_2NdN(SiMe_3)_2$ and $(Me_5C_5)Nd[N(SiMe_3)_2]_2$ have been obtained from reaction of $[Li(OEt_2)_2][(Me_5C_5)_2NdCl_2]$ and $[Na(OEt_2)_2][(Me_5C_5)NdCl_3]$ with sodium bis(trimethylsilyl)amide in toluene, respectively. The monosilylamides $(Me_5C_5)_2MN(SiMe_3)_2$, where M is Nd or Yb, have infrared spectra identical with that of the related uranium(III) derivative $(Me_5C_5)_2UN(SiMe_3)_2$.[16]

Experimental Section

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. Metal chlorides were dried by refluxing over thionyl chloride.

Sodium (Pentamethylcyclopentadienyl)trichlorobis(diethyl ether)neodymate(III). Sodium pentamethylcyclopentadienide[21] (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 × 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 7.4 g (62%).

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 under vacuum, and the residue was extracted with diethyl ether (2 × 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.

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 $[Li(OEt_2)_2][(Me_5C_5)_2NdCl_2]$ (0.58 g, 0.00091 mol) in diethyl ether (30 mL). After 3 h of stirring, the volatile material was removed under 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 under vacuum.

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 8 h of refluxing, the tetrahydrofuran was removed under vacuum and the residue was extracted with diethyl ether (2 × 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.

Bis(pentamethylcyclopentadienyl)chloro(tetrahydrofuran)neodymium(III). The mother liquor from the above reaction was concentrated to ca. 20 mL. Cooling (−10 °C) yielded green prisms (1.7 g, 23%). The ^1H NMR spectrum (36 °C, PhH-d_6 at 90 MHz) consisted of a broad resonance ($\nu_{1/2} = 75$ Hz) at δ 2.95 due to the Me_5C_5 group. The THF resonances were not observed. Futher, the $^{13}C\{^1H\}$ spectrum could not be observed at 36 °C.

The neutral species $(Me_5C_5)_2NdCl(THF)$ may also be prepared by extraction of the residue from reaction of $NaMe_5C_5$ (2 molar equiv) and $NdCl_3$ in tetrahydrofuran with pentane in 10% yield. The complex was identified by IR and melting point.

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 8 h of refluxing, 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 the orange solution stirred for 2 h, the volatile material was removed under vacuum. The residue was washed with pentane (20 mL) and 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 and then evaporated to dryness in vacuum. The residue was extracted with diethyl ether (2 × 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 under vacuum. The yield was 36% (2.9 g). The ^{1}H NMR spectrum (PhH-d_6, 26 °C) consisted of a singlet at δ 7.27, a quartet centered at δ 3.35 (J = 7 Hz), and a triplet centered at δ 1.20 (J = 7 Hz) in area ratio 30:4:6 due to Me_5C_5, $MeCH_2O$, and $MeCH_2O$, respectively. The resonances are narrow, $\nu_{1/2}$ being ca. 1 Hz.

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 $[Na(OEt_2)][(Me_5C_5)_2SmCl_2]$ (0.80 g, 0.0014 mol) in diethyl ether (15 mL). The yellow precipitate was stirred for 1 h and 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 refluxed for 6 h. Tetrahydrofuran was removed under vacuum, and the residue was extracted with diethyl ether (2 × 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 $[Li(OEt_2)_2][(Me_5C_5)_2YbCl_2]$ (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 vacuo. 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 × 100 mL). The purple extracts were concentrated to ca. 100 mL and cooled (−10 °C). The violet prisms were collected and dried under vacuum; yield 2.7 g (33%). A sample was dissolved in benzene and hydrolyzed with water. Examination of the benzene extract (^{1}H NMR) showed only resonances due to diethyl ether and Me_5C_5H.

Bis(pentamethylcyclopentadienyl)chloro(tetrahydrofuran)ytterbium(III). (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 42% (2.8 g). The mass spectrum contained a $(M - THF)^+$ peak at m/e 479; $(Me_5C_5)_2{}^{174}Yb^{35}Cl$ requires m/e 479. A sample was dissolved in benzene and hydrolyzed with water. Examination of the benzene extract (^{1}H NMR) showed only resonances due to tetrahydrofuran and Me_5C_5H.

(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 × 100 mL). The extracts were combined, concentrated to ca. 70 mL, and cooled (−10 °C). The violet needles were collected, dried under vacuum, and identified by melting point and IR spectra; yield 5.2 g (63%).

(c) From $[Na(OEt_2)_2][(Me_5C_5)_2YbCl_2]$. 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 melting point and IR spectra were identical with those of an authentic specimen.

(d) From Dichloromethane. Dichloromethane (0.50 mL, 7.8 mmol) was added to a toluene solution (20 mL) of $(Me_5C_5)_2Yb(THF)\cdot{}^1/_2(PhMe)$ (0.66 g, 0.0012 mol) cooled to 0 °C. After 30 min of stirring at 0 °C, the volatile material was evaporated and the residue crystallized from toluene (ca. 8 mL, −10 °C), in 70% (0.45 g) yield. The melting point and IR spectra were identical with those of the authentic specimen.

(e) From Ytterbium Trichloride. The $(Me_5C_5)_2Yb(THF)\cdot{}^1/_2(PhMe)$ (0.52 g, 0.000 93 mol), dissolved in toluene (30 mL), was added to a suspension of ytterbium trichloride (0.26 g, 0.000 93 mol) in toluene (15 mL). After 12 h of stirring, the solution was filtered, concentrated to ca. 10 mL, and cooled (−10 °C). The violet crystals (0.30 g, 59%) were identified by their melting point and IR spectra. The ^{1}H NMR spectrum consisted of a broad resonance ($\nu_{1/2}$ = 60 Hz) due to the Me_5C_5 group at δ 3.40 (36 °C, PhH-d_6, 90 MHz). The resonances due to THF were not observed.

Bis(pentamethylcyclopentadienyl)chloro(pyridine)ytterbium(III). Pyridine (1 mL, an excess) was added to $(Me_5C_5)_2YbCl(THF)$ (0.84 g, 0.0015 mol) dissolved in diethyl ether (10 mL). After 2 h of stirring, the volatile material was removed in vacuo, and the residue was crystallized from diethyl ether (ca. 20 mL, −10 °C) as purple prisms in 47% (0.40 g) yield.

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 $[Na(OEt_2)_2][(Me_5C_5)_2YbCl_2]$ (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 × 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 $[Li(OEt_2)_2][(Me_5C_5)_2NdCl_2]$ (0.55 g, 0.00086 mol). The mixture was stirred for 8 h, toluene was removed under vacuum, and the residue was extracted with pentane (2 × 20 mL). The extracts were combined, concentrated to ca. 13 mL, and cooled (−10 °C). The large, blue needles were collected and dried under vacuum; yield 0.25 g.

(Pentamethylcyclopentadienyl)bis[bis(trimethylsilyl)amido]neodymium(III). Sodium bis(trimethylsilyl)amide (0.72 g, 0.0039 mol) in toluene (50 mL) was added to $[Na(OEt_2)_2][(Me_2C_5)NdCl_3]$ (1.1 g, 0.0019 mol) in toluene (10 mL). The mixture was stirred for 12 h and 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.

Bis(pentamethylcyclopentadienyl)[bis(trimethylsilyl)amido]ytterbium(III). Sodium bis(trimethylsilyl)amide (0.21 g, 0.0011 mol) in diethyl ether (30 mL) was added to bis(pentamethylcyclopentadienyl)(chloro)(pyridine)ytterbium (0.64 g, 0.0011 mol) in diethyl ether (20 mL). After 10 h of stirring, the volatile material was removed under reduced pressure and the residue was extracted with pentane (50 mL). After filtration, the filtrate was evaporated to ca. 10 mL. Cooling (−10 °C) afforded large, purple prisms in 61% (0.42 g) yield.

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Registry No. $[Na(OEt_2)_2][(Me_5C_5)NdCl_3]$, 78128-13-9; $[Li(OEt_2)_2][(Me_5C_5)_2NdCl_2]$, 78128-14-0; $[Li(tmed)_2][(Me_5C_5)_2NdCl_2]$, 78088-91-2; $[Na(OEt_2)][(Me_5C_5)_2NdCl_2]$, 78128-15-1; $[Li(tmed)][(Me_5C_5)_2SmCl_2]$, 78128-17-3; $[Na(OEt_2)][(Me_5C_5)_2SmCl_2]$, 78128-18-4; $[Na(tmed)][(Me_5C_5)_2SmCl_2]$, 78168-25-9; $[Li(OEt_2)_2][(Me_5C_5)_2YbCl_2]$, 78128-04-8; $[Li(tmed)][(Me_5C_5)_2YbCl_2]$, 78128-20-8; $[Na(OEt_2)_2][(Me_5C_5)_2YbCl_2]$, 78128-21-9; $[Na(tmed)][(Me_5C_5)_2YbCl_2]$, 78128-19-5; $(Me_5C_5)_2YbCl(THF)$, 78064-47-8; $(Me_5C_5)_2YbCl(py)$, 78064-48-9; $(Me_5C_5)_2NdN(SiMe_3)_2$, 78064-49-0; $(Me_5C_5)Nd[N(SiMe_3)_2]_2$, 78064-50-3; $(Me_5C_5)_2NdCl(THF)$, 78064-51-4; $(Me_5C_5)_2YbN(SiMe_3)_2$, 78064-52-5; $(Me_5C_5)_2Yb(THF)$, 74282-46-5.