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STUDIES ON ORGANOLANTHANIDE COMPLEXES

III *. THE STABILIZATION OF EARLY LANTHANOCENE CHLORIDES BY USING A RING-BRIDGED DICYCLOPENTADIENE LIGAND **

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Summary

THF-solvated early lanthanocene chlorides containing ring-bridged dicyclopentadiene as a ligand $[C_5H_4(CH_2)_3C_5H_4]LnCl \cdot THF$ (Ln = Nd, Pr) were synthesized. The disproportionation of dicyclopentadienyl lanthanide chlorides is thus successfully prevented and the stabilization of early lanthanocene chloride achieved. In order to further demonstrate that the products obtained are tetrahydrofuran-solvated, similar complexes of Gd, Dy, Ho, Er, Yb and Lu were also synthesized and characterized. The products obtained are without exception coordinated with one molecular tetrahydrofuran. When the tetrahydrofuran coordinated lanthanocene chlorides were allowed to react with 2,2′-bipyridyl, the coordinated tetrahydrofuran was replaced by 2,2′-bipyridyl in each case to form the 2,2′-bipyridyl complex. The latter are more stable towards air and moisture than the former ones. Fifteen new complexes were synthesized and their structures were verified by elemental analyses, infrared spectra, mass spectra and ^1H NMR. Moreover, the variable temperature (77–291 K) magnetic susceptibilities were also measured.

Introduction

Dicyclopentadienyl lanthanide chlorides, $(C_5H_5)_2LnCl$, are of great importance in the synthetic chemistry of organolanthanides. They are key intermediates for the synthesis of the compounds containing Ln–C σ-bonds [1], Ln–N σ-bonds and Ln–O bonds. Owing to the absence of extensive interactions between 4*f* orbital and ligand

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* Part I, see ref. 1; Part II, see ref. 2.

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orbitals, the stabilization effects caused by ligand field are at best minimal, thus there is a considerable degree of flexibility in the coordination geometries adopted by the complexes and in ligand exchange reactions. Probably due to the lanthanide contraction effect, the early lanthanocene chloride complexes particularly for La, Ce, Pr and Nd have not yet been synthesized [3,4,5].

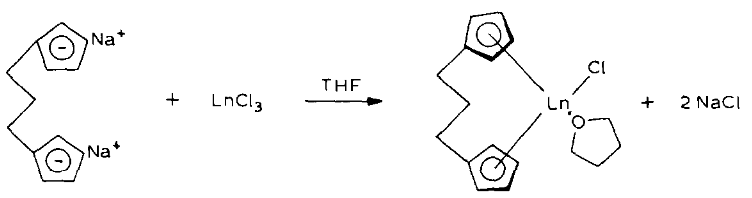
Recently, some organometallic chemists have made efforts to study how to stabilize the dicyclopentadienyl early lanthanide chlorides. By using a bulky pentamethylcyclopentadienyl instead of cyclopentadienyl as a ligand, Evans et al. [6] succeeded for the first time in stabilizing dicyclopentadienyl lanthanide chlorides and obtained bis-pentamethylcyclopentadienyl neodymium chloride as a lithium salt of anionic complex, $[Li(THF)_2][(C_5Me_5)_2NdCl_2]$. Andersen et al. [7] reported that after the sodium salt of pentamethylcyclopentadienyl reacted with $NdCl_3$, the crude products were recrystallized in diethyl ether and two compounds, sodium salt of an anionic complex $[Na(OEt_2)_2][(C_5Me_5)_2NdCl_2]$ and the tetrahydrofuran coordinated neutral complex $(C_5Me_5)_2NdCl \cdot THF$ were obtained. Using di(trimethylsilyl)cyclopentadienyl as a ligand, Lappert et al. [8,9] succeeded in stabilizing early (f^0–f^3) lanthanocene chlorides generating an anionic complex $[Li(THF)_2]$-$[\{C_5H_3(SiMe_3)_2\}_2LnCl_2]$. The solvent free dimeric neutral complexes, $[\{C_5H_3(SiMe_3)_2\}_2LnCl]_2$ were obtained by the sublimation of the anionic complex. Heptamethylindenyl [10] and tetrahydroindenyl [11] were also used to stabilize lanthanocene chlorides (lanthanum and neodymium). Marks [12] reported that dicyclopentadienyl uranium dichloride was stabilized by using ring-bridged dicyclopentadienyl as a ligand.

The authors of this paper, in collaboration with Tsutsui, have used ring-bridged dicyclopentadiene to stabilize early lanthanocene chlorides [2]. Tsutsui et al. [13] synthesized the 1,1′-trimethylenedicyclopentadienyl lanthanum and cerium chlorides and claimed that these chlorides were solvent free neutral complexes. However, Changtao Qian et al. [2] synthesized the 1,1′-trimethylenedicyclopentadienyl praseodymium and neodymium chlorides and obtained tetrahydrofuran coordinated neutral complexes. Because our results are different from Tsutsui's, we further synthesized six 1,1′-trimethylenedicyclopentadienyl lanthanide chlorides (Ln = Gd, Dy, Ho, Er, Yb and Lu). All the products so far obtained were found to be tetrahydrofuran coordinated neutral complexes $[C_5H_4(CH_2)_3C_5H_4]LnCl \cdot THF$ without exception. At the same time, we found that the coordinated-tetrahydrofuran could be replaced by 2,2′-bipyridyl to afford 2,2′-bipyridyl complexes which exhibit better stability to air and moisture.

Results and discussion

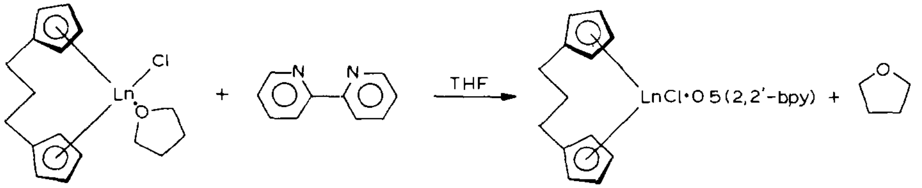
Anhydrous lanthanide chlorides, $LnCl_3$, reacted with disodium salt of 1,3-dicyclopentadienylpropane in THF at −50°C to give tetrahydrofuran-coordinated 1,1′-trimethylenedicyclopentadienyl lanthanide chlorides. The tetrahydrofuran-coordinated 1,1′-trimethylenedicyclopentadienyl lanthanide chlorides were allowed to react with 2,2′-bipyridyl, the tetrahydrofuran was replaced by 2,2′-bipyridyl affording the 2,2′-bipyridyl coordinated complexes as depicted in eqs. 1 and 2.

The physical properties and elemental analyses of the aforementioned eight



(1)

Ln = Pr(1), Nd(2), Gd(3), Dy(4), Ho(5), Er(6), Yb(7), Lu(8)



(2)

Ln = Pr(9), Nd(10), Dy(11), Ho(12), Er(13), Yb(14), Lu(15)

THF-solvated complexes are listed in Table 1 and those of seven 2,2′-bipyridyl coordinated complexes are listed in Table 2.

THF-solvated ring-bridged dicyclopentadienyl lanthanide chlorides $[C_5H_4(CH_2)_3C_5H_4]LnCl\cdot THF$, *1–8*

The elemental analyses of these compounds were consistent with their structures. Thermoanalysis (TG) of **6** (Ln = Er) and **7** (Ln = Yb) complexes were carried out from 60 to 300°C and the weight loss was equal to 17.8 and 16.2%, respectively, consistent with the loss of one mole of tetrahydrofuran. The complexes **6** and **7** were digested by concentrated sulfuric acid, and emission spectrum analysis indicated that

TABLE 1

PHYSICAL PROPERTIES OF $[C_5H_4(CH_2)_3C_5H_4]LnCl\cdot THF$ COMPLEXES **1–8**

Compound	Color	Decomp. temp. (°C)	Yield (%)	Analysis (Found (calcd.) (%))		
				Ln	Cl	O
1 (Pr)	pale-yellow	187–190	31	34.66 (33.65)	7.86 (8.48)	3.20 (3.82)
2 (Nd)	blue-green	142–146	42	36.34 (34.17)	7.51 (8.41)	2.32 (3.79)
3 (Gd)	pale-yellow	155–160	59	36.32 (36.13)	8.49 (8.16)	3.14 (3.68)
4 (Dy)	orange-yellow	150–154	37	36.14 (36.90)	8.80 (8.06)	3.25 (3.63)
5 (Ho)	yellow	170–174	62	38.27 (37.26)	7.54 (8.02)	3.95 (3.61)
6 (Er)	orange-red	140–142	39	37.29 (37.57)	8.83 (7.98)	3.83 (3.60)
7 (Yb)	red	145–150	70	36.84 (38.38)	7.03 (7.87)	2.92 (3.50)
8 (Lu)	pale-yellow	153–160	57	38.53 (38.63)	7.14 (7.84)	3.12 (3.53)

TABLE 2

PHYSICAL PROPERTIES OF $[C_5H_4(CH_2)_3C_5H_4]LnCl\cdot 0.5(2,2'\text{-bpy})$ COMPLEXES **9**–**15**

Compound (Ln =)	Color	Decomp. temp. (°C)	Yield (%)	Analysis (Found (calcd.) (%))		
				Ln	Cl	N
9 (Pr)	yellow	170–175	59	33.07	7.89	3.03
				(33.17)	(8.36)	(3.30)
10 (Nd)	pale-yellow	138–142	41	36.81	7.11	3.44
				(33.69)	(8.29)	(3.27)
11 (Dy)	yellow	168–172	66	36.28	8.13	3.19
				(36.41)	(7.94)	(3.14)
12 (Ho)	yellow	158–160	26	37.18	7.26	2.97
				(36.76)	(7.91)	(3.12)
13 (Er)	orange-yellow	160–164	88	36.80	7.84	3.44
				(37.09)	(7.87)	(3.10)
14 (Yb)	orange-yellow	147–152	29	38.25	8.32	3.16
				(37.87)	(7.78)	(3.06)
15 (Lu)	pale-yellow	153–160	68	38.36	8.38	3.15
				(38.14)	(7.74)	(3.05)

the complexes contained only a trace of sodium. Thus the possibility for sodium salt form of an anionic complex was excluded, and they are neutral complexes.

Except for lanthanum and lutetium, all lanthanides are paramagnetic. Therefore, the ^1H NMR spectrum of **8** was measured using perdeuterotetrahydrofuran as solvent. The results are listed in Table 3. For comparison, the data of ^1H NMR of similar complexes of lanthanum, cerium and Group IVB elements reported previously in the literature are also listed in Table 3.

From Table 3 we can see that the splitting of ring protons of Group IVB compounds into two multiplets has been attributed to the tilting of the rings in the case of bridged derivatives. The $\Delta\delta$ value between two multiplets not only related to the solvent, but also depended on ring–ring angle. In the case of analogous titanocene compound, the $\Delta\delta$ value is only 0.04 ppm in deuterochloroform but the $\Delta\delta$ value was increased to 0.60 ppm in perdeuterobenzene because of the interaction of ring currents of the solvent. On the other hand, some correlation has been found between the degree of ring tilting and the magnitude of the proton splitting. The $\Delta\delta$

TABLE 3

NMR PROTON SHIFTS [a] (δ, TMS, ppm, 25°C)

Compound	Ring protons	Methylene protons	THF protons	Ref.
$[C_5H_4(CH_2)_3C_5H_4]LuCl\cdot THF$ [b]	6.25(s), 5.85(s)	2.80(m), 2.47(m)	3.50(m), 1.63(m)	
$[C_5H_4(CH_2)_3C_5H_4]LaCl$ [c]	5.95(s), 5.78(s)			13
$[C_5H_4(CH_2)_3C_5H_4]LaCl$ [d]	5.98(s), 5.79(s)	2.75(m), 2.45(m)		13
$[C_5H_4(CH_2)_3C_5H_4]CeCl$ [c]	5.65(bm)			13
$[C_5H_4(CH_2)_3C_5H_4]CeCl$ [d]	6.6(bm)	2.75(bm)		13
$[C_5H_4(CH_2)_3C_5H_4]TiCl_2$ [d]	6.49–6.45(m)	2.5(m), 2.2(m)		14
$[C_5H_4(CH_2)_3C_5H_4]TiCl_2$ [e]	6.39(m), 5.79(m)	1.7(m), 1.3(m)		14
$[C_5H_4(CH_2)_3C_5H_4]ZrCl_2$ [e]	6.27(m), 5.72(m)	1.8(m), 1.4(m)		14
$[C_5H_4(CH_2)_3C_5H_4]HfCl_2$ [e]	6.18(m), 5.66(m)	3.9(m), 1.4(m)		14

[a] s = singlet, m = multiplet, bm = broad multiplet. [b] In perdeuterotetrahydrofuran. [c] In THF. [d] In deuterochloroform. [e] In perdeuterobenzene.

TABLE 4

IR DATA OF $[C_5H_4(CH_2)_3C_5H_4]LnCl \cdot THF$ COMPLEXES **1**-**8** (4000-200 cm^{-1})[a]

Compound	**1** (Pr)	**2** (Nd)	**3** (Gd)	**4** (Dy)	**5** (Ho)	**6** (Er)	**7** (Yb)	**8** (Lu)
Low-frequency region	210s	220s	215s	230s	230s	230s	230s	235s
	250m	250m	250m	250m	250m	250m	250m	260m
	400m	365s	390m	405m	388s	390m	390m	388s
	465w	490m	400w	470m	465w	465w	465w	460w
Coordinated-THF	870m	875m	862m	862m	863m	864m	862m	862m
	1045s	1050s	1052m	1050s	1050s	1050s	1050s	1045m
Cyclopentadienyl	772s	770s	770vs	775vs	775vs	775vs	778vs	775vs
	1024s	1029s	1022s	1015s	1015s	1015s	1015s	1010s
	1440s	1440s	1443s	1442s	1442s	1440s	1444s	1440s
	3070m	3060s	3090s	3080s	3070s	3080s	3080s	3070s
Methylene	2880vs	2870vs	2880vs	2880vs	2880vs	2880vs	2880vs	2860vs
	2930vs	2930vs	2930vs	2920vs	2920vs	2916vs	2920vs	2920vs

[a] w: weak; m: medium; s: strong; vs: very strong; sh: shoulder.

value becomes greater with the increase of the ring–ring angle and is changed to small value with decreasing of the ring–ring angle. It is unfortunate that owing to the low solubilities of lanthanocene chlorides in perdeuterobenzene we are not able to deduce the magnitude of the ring–ring angle on the basis of the $\Delta\delta$ value.

The infrared spectra of eight compounds mentioned above were measured from 4000 to 200 cm^{-1}. The spectral features of these compounds are very similar. The data of major absorption peaks are listed in Table 4.

The complexes exhibit four characteristic absorption peaks in the low frequency region, and the absorption peak at about 250 cm^{-1} was tentatively assigned as a characteristic absorption of π-bonded cyclopentadienyl group to Ln metal. The assignment of the characteristic absorption peaks of Ln–Cl bonds at low frequency region needs further investigation. The characteristic absorption peaks of the coordinated tetrahydrofuran appear at about 862–875 and 1045 cm^{-1}, respectively. All complexes exhibit four characteristic cyclopentadienyl absorptions at about 770, 1015, 1440 and 3080 cm^{-1} and two characteristic methylene absorptions at 2880 and 2930 cm^{-1}. Thus all characteristic absorption peaks of coordinating tetrahydrofuran, ring-bridged methylene and cyclopentadienyl are evidently present. Comparing the infrared spectra of dicyclopentadienyl lanthanide chlorides with 1,1′-trimethylenedicyclopentadienyl lanthanide chlorides, it was found that a remarkable difference appears at the olefinic C–H stretching region (3000–3100 cm^{-1}). The latter exhibits only a single peak of strong intensity at this region, indicating that the cyclopentadienyl is η^5-bonded to the metal in these complexes, while the bis-η^5-cyclopentadienyl lanthanide chlorides exhibit multiple peaks at 3000–3100 cm^{-1}.

The magnetic susceptibilities of complexes **1** to **7** were determined at variable temperature (77–291 K). The effective magnetic moments which were obtained from the treatment of experimental results according to the Curie-Weiss rule are listed in Table 5.

The effective magnetic moments of these complexes except **6** are close to the value of the trivalent state of lanthanide. Therefore, the oxidation state of lanthanide ion is positive three in each case, and the results also show the lack of evident magnetic

TABLE 5

MAGNETIC PROPERTIES OF $[C_5H_4(CH_2)_3C_5H_4]LnCl \cdot THF$ COMPLEXES 1–7

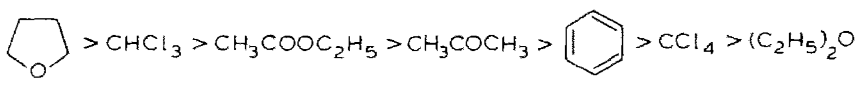
Compound	θ (K)	μ_{eff} (BM) (obsd.)			μ_{eff} (BM) (theor.) [15]	Range of μ_{eff} (BM) [16] [a]
		77 K	195 K	291 K		
1 (Pr)	−2.0	3.45	3.50	3.50	3.62	3.41–3.62
2 (Nd)	−2.0	3.33	3.33	3.33	3 68	3.43–3.62
3 (Gd)	−1.9	8.13	8.17	8.15	7.94	7.46–8.1
4 (Dy)	−1.2	11.25	11.31	11.32	10.6	10.0–10.9
5 (Ho)	11.0	10.88	10.90	10.90	10.6	10.1–10.5
6 (Er)	19.8	10.56	10.56	10.59	9.6	9.0–9.55
7 (Yb)	11.8	4.12	4.15	4.12	4.5	4.3–4.6

[a] The observed values which were reported in literatures.

coupling interaction between lanthanide metals. The effective magnetic moments of these complexes are temperature-independent, in agreement with that for dicyclopentadienyl lanthanide chlorides. However, these results are quite different from the results reported by Tsutsui [13], who suggested that the effective magnetic moment of $[C_5H_4(CH_2)_3C_5H_4]CeCl$ is dependent on the temperature.

The mass spectra of **1**, **6** and **7** did not show a parent molecular ion. However, they showed tetrahydrofuran, 1,1′-trimethylenedicyclopentadienyl, cyclopentadienylpropane, cyclopentadienyl ion and fragments which may be attributed to the moieties containing the above mentioned groups connected with the metal.

The order of the solubility of **6** in some solvents is shown as follows:



It is interesting to note that the solubility of **6** in organic solvents containing oxygen seems to be related to the complexing ability of lanthanide [17,18].

By using a ring-bridged dicyclopentadiene instead of separated cyclopentadiene as a ligand, the disproportionation of the early lanthanocene chlorides is thus prevented, the stabilization of early lanthanocene chlorides achieved, and the early lanthanocene chlorides can be isolated. These complexes are still extremely sensitive to air and moisture and decompose rapidly upon exposure to air.

2,2′-Bipyridyl-coordinated ring-bridged dicyclopentadienyl lanthanide chlorides $[C_5H_4(CH_2)_3C_5H_4]LnCl \cdot 0.5(bpy)$, ***9–15***

Although the tetrahydrofuran coordinated ring-bridged dicyclopentadienyl lanthanide chlorides can be isolated, they are still extremely sensitive to air and moisture.

In order to improve the stability, the THF-coordinated ring-bridged dicyclopentadienyl lanthanide chlorides were allowed to react with 2,2′-bipyridyl. The coordinated tetrahydrofuran was thus replaced by 2,2′-bipyridyl in each case giving 2,2′-bipyridyl complexes as shown in eq. 2. It should be noted that even when the molar ratios of chlorides to 2,2′-bipyridyl in starting material were changed from 1/1 to 1/2, the atomic ratios of lanthanide metal to nitrogen in products always were 1/1. In other words, one metal atom coordinated only with one nitrogen atom

TABLE 6

IR DATA OF SEVEN NEW COMPLEXES (**9–15**) $[C_5H_4(CH_2)_3C_5H_4]LnCl \cdot 0.5(2,2'\text{-bpy})$

Compound	2,2′-bpy	**9** (Pr)	**10** (Nd)	**11** (Dy)	**12** (Ho)	**13** (Er)	**14** (Yb)	**15** (Lu)
Low frequency region		200s	200s	215s	220s	212s	220s	220s
		235m	240m	230m	235m	240m	245m	240m
		340s	345s	350m	390m	352m	395m	395m
Pyridine ring	408s	410m	410m	416m	416m	416m	420m	417s
	621s	640s	641m	646m	646m	646m	650m	647m
	994s	1004m	1005m	1006m	1006m	1008m	1010m	1010m
	1580s	1596s	1596s	1597s	1598s	1597s	1600s	1602s
Cyclopenta-dienyl		760vs	760vs	765vs	765vs	765vs	770vs	765vs
		1007m	1012s	1016s	1015s	1015s	1020s	1018s
		1434s	1435s	1437s	1437s	1440s	1440s	1440s
		3070s	3060s	3070s	3070s	3070s	3070s	3070s
Methylene		2860s	2860s	2860s	2860s	2850s	2860s	2860s
		2920vs	2920vs	2930vs	2930vs	2930vs	2935vs	2928vs

of pyridine ring, and the coordination number in the bipyridyl complexes is eight, which is the same as THF solvated complexes. The solubility of these 2,2′-bipyridyl complexes in tetrahydrofuran is evidently decreased, and they were precipitated as yellow solids from the solution. Some physical properties are listed in Table 2.

The elemental analyses of these compounds were consistent with their structures showing that they contain no oxygen.

The infrared spectra of 2,2′-bipyridyl complexes from 200 to 4000 cm^{-1} were determined. Four characteristic cyclopentadienyl absorptions and two characteristic absorption peaks of the methylene groups are still apparently present. All the characteristic absorption peaks of the pyridine ring appear and the characteristic peaks of coordinated tetrahydrofuran disappear. The major infrared spectra data of seven new 2,2′-bipyridyl complexes are listed in Table 6.

After forming 2,2′-bipyridyl complexes, the absorption peaks at low frequency such as at 230 and 250 cm^{-1}, which arise from the original complexes, all shift to lower frequencies. On the contrary, four characteristic absorption peaks of the pyridine ring at 408 cm^{-1} (out-of-plane ring deformation vibration), 621 cm^{-1} (in-plane ring deformation vibration), 994 cm^{-1} (pyridine ring breathing vibration) and 1580 cm^{-1} (pyridine ring deformation vibration) all shift to higher frequencies as compared with those in $[C_5H_4(CH_2)_3C_5H_4]LnCl \cdot 0.5(2,2'\text{-bpy})$. This implies that a pair of electrons on nitrogen is coordinated to the metal to form a coordinate covalent bond. It was also found that the $\Delta\nu$ values increased with an enlargement in atomic number of the lanthanide. It seems that the complexation interaction increased with a decrease in ionic radius of Ln^{3+}. The relation of $\Delta\nu$ with atomic number of Ln^{3+} is depicted in Fig. 1.

The magnetic susceptibilities of six 2,2′-bipyridyl complexes were determined at variable temperature (77–291 K). The effective magnetic moments which were obtained from the treatment of experimental results according to the Curie-Weiss rule are shown in Table 7.

The effective magnetic moments of these complexes except **9** and **14** are close to the value of the trivalent state of lanthanide and temperature-independent. These

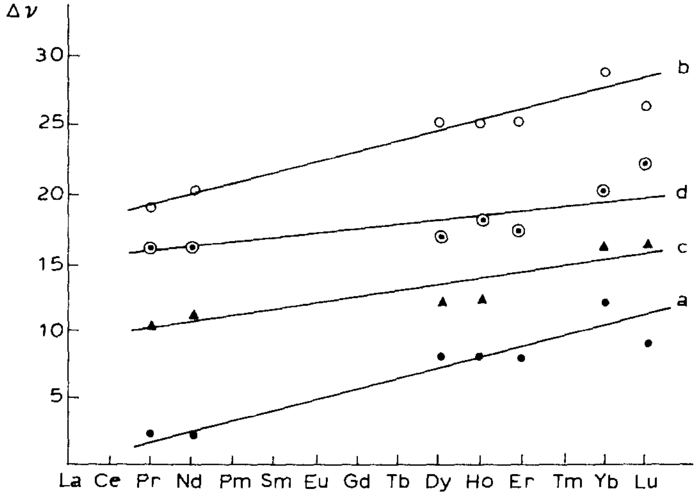


Fig. 1. The relation of Δν with atomic number of Ln^{3+}. a) 408 cm^{-1}; b) 621 cm^{-1}, c) 994 cm^{-1}; d) 1580 cm^{-1}.

results are in agreement with the effective magnetic moment of μ-pyrazinebis(tris(cyclopentadienide)ytterbium(III)] reported by Raymond [19]. However, the effective magnetic moments of **9** and **14** are higher than the normal value.

The stabilities of all 2,2′-bipyridyl coordinated 1,1′-trimethylenedicyclopentadienyl lanthanide chlorides produced by the replacement of tetrahydrofuran with

TABLE 7

MAGNETIC PROPERTIES OF THE $[C_5H_4(CH_2)_3C_5H_4]LnCl \cdot 0.5(2,2'\text{-bpy})$ COMPLEXES **9–14**

Compound	Temperature (K)	χ_m ($\times 10^6$ cgsu)	θ (K)	μ_{eff} (BM)
	77	27248		4.29
9 (Pr)	195	11468	7.2	4.30
	291	7770		4.30
	77	19268		3.63
10 (Nd)	195	8299	8.3	3.66
	291	5643		3.68
	77	196463		10.86
11 (Dy)	195	77042	−1.9	10.90
	291	51546		10.93
	77	197533		10.67
12 (Ho)	195	72254	2.2	10.68
	291	49020		10.72
	77	134952		9.26
13 (Er)	195	54915	2.4	9.31
	291	36900		9.31
	77	35336		5.63
14 (Yb)	195	17391	35	5.66
	291	12232		5.65

2,2′-bipyridyl were evidently improved. They could withstand exposure to air (22°C, relative humidity: 50%) for about 1 h without appreciable change in color.

In order to compare the stability, infrared spectra of $[C_5H_4(CH_2)_3C_5H_4]DyCl \cdot THF$ (**4**) and $[C_5H_4(CH_2)_3C_5H_4]DyCl \cdot 0.5(bpy)$ (**11**) were measured under the same conditions. When the mulls for the measurement of the infrared spectra were prepared in air, the infrared spectra showed that the complex **4** was seriously hydrolyzed, the intensity of four characteristic cyclopentadienyl absorptions all weakened greatly and the characteristic hydroxy absorptions appeared at 1635 and 3300–3400 cm^{-1} with strong intensity. However, under the same conditions four characteristic cyclopentadienyl absorptions and all characteristic absorption peaks of pyridine ring of complex **11** were very clear, the intensity of peaks did not change remarkably, but weak hydroxy absorptions were also observed. The infrared spectra of mulls which were prepared after 60 min upon exposure to air showed that the four characteristic cyclopentadienyl absorptions for complex **4** all had disappeared, but the four characteristic cyclopentadienyl absorption peaks for complex **11** all remained without appreciable decrease in intensity. The stability of complex **11** is certainly higher than that of complex **4**. In conclusion, the stability of ring-bridged dicyclopentadienyl lanthanide chlorides to air and moisture is obviously improved with 2,2′-bipyridyl coordination.

Experimental

All operations on these organolanthanide complexes were performed in an atmosphere of prepurified argon by using Schlenk techniques or in a glovebox. All solvents were refluxed and distilled over either finely divided $LiAlH_4$ or blue sodium benzophenone under argon immediately prior to use. Anhydrous lanthanide chlorides are prepared from the hydrates by a literature method [1]. Melting points and thermal decomposition temperatures were determined in sealed argon filled capillaries and were uncorrected. Infrared spectra were recorded on Perkin–Elmer 580B spectrometers as Nujol and Fluorolube mulls and were examined between disk-shaped CsI crystal plates; the mulls were prepared in an argon filled glovebox. The solid state magnetic susceptibility measurements were performed as previously described [1]. ^1H NMR spectra are obtained on EM 360 L (60 MHz) spectrometer and are referenced to external Me_4Si. THF-d_8 (E. Merck for NMR spectroscopy) was dried by treatment with Na/K alloy. Trap-to-trap distillation followed by several cycles of freeze-thaw degassing were used to remove the final traces of gases from this solvent. Mass spectra were recorded on a Finnigan 4021 spectrometer.

Metal analyses of lanthanides were accomplished using direct complexometric titration procedure with disodium EDTA [1].

A microdetermination of oxygen in organolanthanide complexes was accomplished by using photo-coulometric titration [20]. This process involves a flash pyrolysis of the organolanthanide complexes under nitrogen at 900°C. The oxidative products, after passing through a platinum carbon filling heated at 900–950°C, are reduced to carbon monoxide, which is further oxidized to carbon dioxide on copper oxide at 350°C. Finally, carbon dioxide is determined by photo-coulometric titration with a constant current of 20 mA. Each analysis takes approximately 15 min and the standard deviations is $\pm 0.5\%$.

1,1′-Trimethylenedicyclopentadienyl praseodymium chloride · THF (1)

C_5H_5Na (0.0304 mol) was prepared in the usual manner from cyclopentadiene and sodium sand in 30 ml of THF at room temperature. The solution was cooled to −5°C and 2.95 g (0.0146 mol) of 1,3-dibromopropane in 20 ml THF was added. The reaction mixture was allowed to stir about 2 h. The mixture was centrifuged and the precipitate was removed from the solution. The pink solution thus obtained was reacted again with sodium sand in 50 ml of THF at 42–48°C for about 24 h. The 100 ml of THF solution containing 0.0146 mol of disodium salt of 1,3-dicyclopentadienylpropane obtained was transferred to a centrifuge Schlenk flask containing 3.44 g (0.0139 mol) of $PrCl_3$ and 30 ml of THF and cooling to −50°C. The reaction mixture was allowed to warm to room temperature and then stirred for 18 h. The Schlenk flask was centrifuged, the precipitate was removed from the solution, and the THF solution was concentrated to about 40 ml. Addition of 80 ml of hexane gave a pale yellow precipitate. After removal of the hexane solution, the product was dried in vacuo and resulted in pale-yellow solid. The yield of 1,1′-trimethylenedicyclopentadienyl praseodymium chloride · THF is 1.8 g (31%). Anal. Found: Pr, 34.66; Cl, 7.86; O, 3.10. $C_{17}H_{22}ClOPr$ calcd.: Pr, 33.65; Cl, 8.48; O, 3.84. Decomposition temperature: 187–190°C. IR (Nujol and Fluorolube), (cm^{-1}) (relative intensity), 210s, 250s, 400m, 465w, 675m, 720m, 772vs, 830m, 870m, 890m, 915w, 1024s, 1045s, 1440s, 1457s, 1600m, 2880vs, 2930vs, 2970(sh,s) 3070m.

Other compounds (**2**, **3**, **4**, **5**, **6**, **7** and **8**) with tetrahydrofuran-coordinated were synthesized in a similar way.

1,1′-Trimethylenedicyclopentadienyl praseodymium chloride · 0.5(2,2′-bpy) (9)

Into a centrifuge Schlenk flask was placed 0.25 g (0.000594 mol) of tetrahydrofuran coordinated 1,1′-trimethylenedicyclopentadienyl praseodymium chloride and 20 ml of THF resulting a yellow-orange solution. Into a dropping funnel was placed 0.093 g (0.000597 mol) of 2,2′-bipyridyl and 5 ml of THF. Then the THF solution of 2,2′-bipyridyl was added dropwise to the THF solution of 1,1′-trimethylenedicyclopentadienyl praseodymium chloride. A yellow precipitate was immediately produced, and reaction was carried out for 2 h at room temperature. The Schlenk flask was centrifuged and the precipitate was dried in vacuo and resulted in yellow solid. The yield of 1,1′-trimethylenedicyclopentadienyl praseodymium chloride · 0.5(2,2′-bpy) is 0.15 g (59%). Anal. Found: Pr, 33.07; Cl, 7.87; N, 3.03. $C_{18}H_{18}ClNPr$ calcd.: Pr, 33.17; Cl, 8.36; N, 3.30. IR (Nujol and Fluorolube), (cm^{-1}) (relative intensity) 200s, 235m, 340s, 410s, 465m, 621m, 640s, 651w, 720w, 737m, 760vs, 810w, 895w, 1004m, 1007s, 1030w, 1060w, 1155m, 1165w, 1240w, 1317w, 1325s, 1435vs, 1455w, 1475m, 1494w, 1567m, 1576m, 1585m, 1596s, 2860vs, 2920vs, 3070s.

Other compounds (**10**, **11**, **12**, **13**, **14** and **15**) with 2,2′-bipyridyl coordinated were synthesized in a similar way.

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