(Pentamethylcyclopentadienyl)ytterbium and -lutetium Complexes by Metal Oxidation and Metathesis

PATRICIA L. WATSON,* JOHN F. WHITNEY, and RICHARD L. HARLOW

Anionic organoytterbium complexes, $Li[YbX_3(C_5Me_5)]$ and $Li[YbX_2(C_5Me_5)_2]$, were obtained by oxidation of ytterbium metal with C_5Me_5I in the presence of LiI (X = I) or by reaction of $YbCl_3$ with LiC_5Me_5 (X = Cl). Analogous lutetium complexes were obtained by similar reactions. Anionic complexes were also obtained for both metals with the use of the less hindered ligand $C_5H_4SiCH_3Ph_2$. The molecular structures of $Li[YbX_2(C_5Me_5)_2](ether)_2$ (X = I, Cl), $Li[YbCl_2-(C_5H_4SiCH_3Ph_2)_2](ether)_2$, and $Yb(C_5Me_5)_2Cl_2AlCl_2$ (determined by X-ray crystallography) all contained planar YbX_2M' (M′ = Li or Al) units with pseudotetrahedral coordination around both Yb and M′.

The organic chemistry of the lanthanide elements has been subject to increasing investigation. Two comprehensive reviews on this subject have been published recently.[1,2] In most cases complexes have been prepared by anionic metathesis reactions with anhydrous lanthanide trihalides (usually chlorides) as the metal reagents. This technique has yielded homoleptic alkyls,[3] phosphides,[4] and amides[5] in addition to mixed-ligand and cyclopentadienyl (C_5H_5) species. Metathesis of the divalent halides of ytterbium[6,7] and europium[7] also provides a route to divalent organometallic complexes.

The direct use of lanthanide metals as reagents for the preparation of organometallic complexes has been quite limited, although they are readily available. Divalent cyclooctatetraenyl[8] and bis(cyclopentadienyl)[9] complexes of ytterbium and europium were obtained by the direct reaction of the respective metals with C_8H_8 or C_5H_6, often in liquid ammonia. Ammonia oxidizes ytterbium to the trivalent state at room temperature.[10a] Oxidation of ytterbium metal to the trivalent state also occurs[10b] with alcohols (to give mainly the tris(alkoxides)) in the presence of mercuric chloride as catalyst. Evans[11] has utilized lanthanide vapors to prepare butadiene derivatives of erbium and neodymium which are thought to be trivalent. The oxidation state of described samarium and lanthanum complexes is less certain. Deacon et al.[12] developed a transmetalation reaction to prepare the first fluorocarbon organolanthanoids from $(R_F)_2Hg$ and ytterbium metal. Solutions of divalent "Grignard-like" reagents were prepared from ytterbium metal and a number of alkyl iodides.[13]

We have prepared a family of ytterbium(II) and -(III) and lutetium(III) halide and alkyl complexes by direct metal oxidation and ligand-for-halide metathesis reactions. The bulky pentamethylcyclopentadienyl (C_5Me_5) anion was used as a supporting ligand to improve crystallinity and to inhibit the formation of dimeric complexes common with lanthanide derivatives of the parent C_5H_5 ligand.[14] These properties have been used to advantage in the chemistry of group 4[15] and actinide[16] elements. Decomposition via ring hydrogen atom abstraction has been noted for the less substituted C_5H_4R complexes of several lanthanides.[17]

The preparation and molecular structures of several halogen-containing C_5Me_5 complexes are presented in this paper. Derivative alkyl complexes and divalent chemistry will be described separately.[18]

Experimental Section

Materials. All manipulations of air- and moisture-sensitive complexes were routinely conducted under inert atmosphere (with the use of a Vacuum Atmospheres He-43 Dri-Lab, or a Schlenk double-manifold system, with nitrogen as inert gas) or on a conventional vacuum line. Glassware was routinely dried at 120 °C under vacuum and cooled in a nitrogen atmosphere prior to use.

Infrared (IR) spectra were recorded on a Perkin-Elmer 283B grating spectrophotometer. Reported spectra are a composite of data from Fluorolube mulls between NaCl plates, Nujol mulls between NaCl plates, and Nujol mulls between polyethylene (down to 200 cm⁻¹ only).

Visible (VIS) spectra were recorded on a Varian Cary 218 spectrophotometer between 750 and 350 nm, using solutions prepared from 120–150 mg (weighed with ±1 mg accuracy) complex diluted to 100 mL with the appropriate solvent. VIS data is reported as VIS (solvent) λ_{max} (extinction coefficient). A Cary 15 spectrophotometer was used on occasion to obtain spectra in the near-IR region from 750 to 1000 nm.

Nuclear magnetic resonance (NMR) spectra were recorded on Varian EM390 (at 90 MHz for ¹H) and Bruker WH-90 (at 22.63 MHz for ¹³C) spectrometers and were referenced to external Me_4Si. Chemical shifts of paramagnetic Yb(III) complexes (0.1 M solutions approximately) are reported in Hz relative to the highest field peak of the THF-d_7 or toluene-d_7 solvent (positive shift is downfield). Widths at half-height ($W_{1/2}$) are given in Hz ±10%.

Melting points were measured in capillaries, sealed under nitrogen, on a Thomas Hoover capillary melting point apparatus and are uncorrected.

Elemental analysis were performed by the Physical and Analytical Division, Central Research and Development Department, E. I. du Pont de Nemours and Co., Experimental Station, Wilmington, DE.

Solvents were distilled under 1 atm nitrogen from an appropriate drying agent. Tetrahydrofuran (THF), dimethoxyethane (DME),

(1) Marks, Tobin *Prog. Inorg. Chem.* **1978**, *24*, 51–107.
(2) Marks, Tobin; Fischer, R. Dieter *NATO Adv. Study Inst. Ser., Ser. C* **1979**, *44*.
(3) Schumann, H.; Müller, J. *J. Organomet. Chem.* **1979**, *169*, C1–C4; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 276; *J. Organomet. Chem.* **1978**, *146*, C5–C7. Wayda, A. L.; Evans, W. J. *J. Am. Chem. Soc.* **1978**, *100*, 7119–7121. Cotton, S. A.; Hart, F. A.; Hursthouse, M. B.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1972**, 1225–1226.
(4) Schumann H.; Frisch, G. *Z. Naturforsch., A* **1979**, *34A*, 748–749.
(5) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021–1023.
(6) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1980**, 652–653.
(7) Tilley; T. Don; Andersen, Richard A. *Inorg. Chem.* **1980**, *19*, 2999–3003. We thank these authors for preliminary communication of their results.
(8) De Kock, C. W.; Ely, S. R.; Hopkins, T. E.; Brault, M. A. *Inorg. Chem.* **1978**, *17*, 625–631. Hayes, R. G.; Thomas, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 6876.
(9) Hayes, R. G.; Thomas, J. L. *Inorg. Chem.* **1969**, *8*, 2521–2522. Fischer, E. O.; Fischer, H. *J. Organomet. Chem.* **1964**, *3*, 181–187.
(10) (a) Salot, S.; Warf, J. C. *J. Am. Chem. Soc.* **1968**, *90*, 1932–1933. C. Hadenfeldt, C.; Jacobs, H.; Juza, R. *Z. Anorg. Allg. Chem.* **1970**, 144–156. Linde, G.; Juza, R. *Ibid.* **1974**, *409*, 199–214. (b) Mazdiyasni, K. S.; Lynch, C. T.; Smith, J. S. *Inorg. Chem.* **1966**, *5*, 342–343.
(11) Evans, W. J.; Engerer, S. C.; Neville, A. C. *J. Am. Chem. Soc.* **1978**, *100*, 331–333. See also: Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1007–1008.
(12) Deacon, G. B.; Koplick, A. J.; Raverty, W. D.; Vince, D. G. *J. Organomet. Chem.* **1979**, *182*, 121–141.
(13) Evans, D. F.; Fazakerly, G. V.; Phillips, R. F. *J. Chem. Soc. A* **1971** 1931–1934.

(14) Maginn, R. E.; Manastyrskyj, S.; Dubeck, M. *J. Am. Chem. Soc.* **1963**, *85*, 672–676.
(15) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121–127 and references therein.
(16) Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Science (Washington, D.C.)* **1979**, *203*, 172–174 and references therein.
(17) Ballard, D. G. H.; Courtis, A.; Holton, J.; McMeeking, J.; Pearce, R. *J. Chem. Soc., Chem. Commun.* **1978**, 994–995.
(18) Watson, P. L.; Whitney, J. F.; Harlow, R. L., manuscript in preparation.

diethyl ether, toluene, and pentane were all dried over Na/benzophenone. Acetonitrile was dried over activated 3-Å molecular sieves. All deuterated solvents were dried over 3-Å molecular sieves (activated at 250 °C under vacuum) and then filtered prior to use.

Pentamethylcyclopentadiene (C_5Me_5H) was prepared by the Special Service Laboratory, Central Research and Development Department, E. I. du Pont de Nemours and Co., Wilmington, DE, according to the procedure of Bercaw and Threlkel.[19] Ytterbium metal, anhydrous ytterbium trichloride, and anhydrous lutetium trichloride were purchased from Cerac, Inc., Milwaukee, WI. Lithium pentamethylcyclopentadiene (LiC_5Me_5) was prepared from *n*-butyllithium and C_5Me_5H in pentane. Potassium pentamethylcyclopentadiene (KC_5Me_5) was prepared from potassium hydride and C_5Me_5H in THF.

Complexes were analyzed for weight percent of C_5Me_5 by hydrolysis and subsequent analysis of C_5Me_5H by gas chromatography. An accurately weighed sample (approximately 0.05 g) was treated with H_2O (20 μL) and methanol (30 μL) in a septum sealed vial. Dodecane (~0.4 mL) was added, and the sample was shaken until colorless. With cyclooctane as an internal standard, the dodecane solution was analyzed with the use of a Perkin-Elmer Sigma 2 gas chromatograph (column: 5% carbowax 20M TPA on 80/100 Chromosorb PAW, 6 ft. × $1/8$ in., at 75 °C, injector 150 °C, flame detector 250 °C.)

C_5Me_5I.[20] A solution of I_2 (2.6 g, 0.010 mol) in ether (50 mL) was added very slowly via syringe to a stirred suspension of LiC_5Me_5 (1.56 g, 0.011 mol) in ether (100 mL), maintained at −78 °C under nitrogen. When the color of I_2 was completely discharged and the color of the solution was pale yellow, the solution was evaporated to dryness at 0 °C and extracted with cold pentane, and the pentane solution was filtered. This extraction procedure was repeated twice. The filtrate was then evaporated to dryness, and the residues were crystallized from a small quantity of ether at −40 °C to give pale golden needles of C_5Me_5I (2.1 g): ^1H NMR (toluene-d_8) δ 1.63 (s, 1 CH_3), 1.72 (s, 2 CH_3), 2.18 (s, 2 CH_3).

Li[YbI$_3$(C$_5$Me$_5$)](ether)$_2$ (1). To a solution of C_5Me_5I and LiI in ether (prepared as above, with no isolation of products) was added Yb metal (40 mesh, 1.9 g, 0.011 mol). The reaction mixture was stirred at room temperature for ~15 h, and the resulting solution was then filtered. The deep green filtrate was evaporated to dryness, extracted with toluene (~30 mL), and then filtered; pentane (~10 mL) was added to the filtrate, and the solution was cooled to −40 °C until the compound precipitated. The product was collected by filtration and dried under vacuum; yield 2.8 g (30% based on LiC_5Me_5; 45% based on I_2). At ~120 °C the complex faded from green to almost white (no melting point below 250 °C): VIS (ether) 420 and 705 nm; VIS (THF) 365; VIS (CH$_3$CN) 610; hydrolysis % C_5Me_5H calcd 16.1 and 17.8 (calculated for 2 or 1 coordinated ethers, respectively), found 18.5. Anal. Calcd for [C$_{18}$H$_{31}$I$_3$LiO$_2$Yb]: C, 25.72; H, 3.72; I, 45.34; Yb, 20.59. Found: C, 25.41; H, 3.93; I, 44.36; Yb, 20.71.

Li[YbI$_2$(C$_5$Me$_5$)$_2$](ether)$_2$ (2). The reaction was repeated exactly as for Li[YbI$_3$(C$_5$Me$_5$)](ether)$_2$ but was stirred for 2 days after the addition of Yb metal. The reaction mixture was filtered. The whitish solid thus obtained (~2 g) was determined to be YbI$_2$(ether) by elemental analysis; the purple filtrate was evaporated to dryness and extracted with toluene. The toluene extracts were filtered, and the filtrate was cooled to −40 °C. The purple solids which precipitated were collected by filtration and dried under vacuum; yield 1.5–2.0 g (~30%). At 145 °C, the color-lightened; at 210 °C the compound turned yellowish (no melting point below 250 °C): IR 2860–3000 (s), 1440 (m), 1380 (m), 1190 (w), 1155 (m), 1090 (m), 1060 (s), 1020 (m), 1000 (m), 900 (m), 835 (w), 785 (w), 730 (w), 390–410 (s), 295 (s), 130 (w) cm^{-1}; VIS (THF) 380 (98), 555 (267), 913 (48), 968 (99), 994 (48) nm; Hydrolysis % C_5Me_5H calcd 31.7, found 30.7; ^1H NMR (THF-d_8) *J* = −8 Hz, $W_{1/2}$ = 30 Hz. Anal. Calcd for [C$_{28}$H$_{50}$I$_2$LiO$_2$Yb]: C, 39.45; H, 5.91; I, 29.77; Yb, 20.30. Found: C, 39.46; H, 5.87; I, 30.16; Yb, 20.58.

Reaction of Yb(0) with C$_5$Me$_5$I. Ytterbium metal (0.173 g, 0.001 mol) and C$_5$Me$_5$I (0.262 g, 0.001 mol) were stirred together in ether (20 mL). After a variable induction period (1–6 h), the solution turned a dull grey and pink YbI$_3$(THF)$_{3,4}$ gradually precipitated. The solution

was filtered after 12 h. The pale yellow solids, YbI$_2$(ether), were recrystallized from THF and identified by elemental analysis. The filtrate was stripped, and the residues were taken up in a small portion of pentane and passed through a short (1 in.) alumina column in a pipet. The eluate was evaporated to dryness and the residues (0.12 g, 90%) were shown to be the dimer (C$_5$Me$_5$)$_2$: ^1H NMR (CDCl$_2$) δ 1.73 (8 CH_3), 1.16 (2 CH_3); ^1H NMR (toluene-d_8) δ 1.94 (4 CH_3), 1.88 (4 CH_3), 1.34 (2 CH_3); ^1H NMR (benzene-d_6) δ 1.80 (4 CH_3), 1.72 (4 CH_3), 1.20 (2 CH_3) (lit.[21] ^1H NMR (benzene-d_6) δ 1.78, 1.70, 1.18 (4:4:2)).

Li[YbCl$_3$(C$_5$Me$_5$)](THF) (3). A suspension of anhydrous YbCl$_3$ (2.0 g, 0.0072 mol) and LiC$_5$Me$_5$ (1.0 g, 0.007 mol; as a very fine powder) in THF (50 mL) was stirred at 20 °C for 2 h. The deep blue solution was evaporated to dryness and extracted with toluene (or diethyl ether); the extracts were filtered, and the filtrate was concentrated to several milliliters. Addition of pentane caused precipitation of the product as a pale blue powder (sometimes cooling or trituration of the product as an oil was necessary to produce solids): yield 2.8g (80%); no melting point below 250 °C; VIS (ether) 606 (105); VIS (THF) 585 (115), 957 (13), 972 (18), 992 (22), 1000 (44) nm; IR 2950–2840 (s), 1440 (m), 1375 (m), 1210 (m), 1035 (m), 1010 (s), 855 (s), 835 (m), 520 (s), 410 (s), 300 (s), 245 (m), 225 (m) cm^{-1}; hydrolysis % C_5Me_5 calcd 27.3, found 25.5. Anal. Calcd for [C$_{14}$H$_{23}$Cl$_3$LiOYb]: C, 34.06; H, 4.69; Cl, 21.54; Yb, 35.05. Found: C, 34.00; H, 4.87; Cl, 21.84; Yb, 35.40.

Li[YbCl$_2$(C$_5$Me$_5$)$_2$](ether)$_2$ (4). A suspension of YbCl$_3$ (10 g, 0.0358 mol) and LiC$_5$Me$_5$ (11 g, 0.0774 mol; as a very fine powder) in THF (250 mL) was refluxed for 4 h and then stirred at 20 °C overnight. The resulting solution was evaporated to complete dryness. Residues were extracted either with toluene (to yield a solution of Li[YbCl$_2$(C$_5$Me$_5$)$_2$](THF)$_2$) or diethyl ether (200 mL). Diethyl ether extracts were filtered, and the filtrate was maintained at −40 °C overnight. The dark purple material which crystallized was collected by filtration and dried briefly in vacuum: first crop 11 g (46%); second crop 6 g (25%) (No melting point below 250 °C); VIS (THF) 510 nm (225); VIS (ether) 520 nm (277); IR (bis(diethyl ether) adduct) 2980, 2880, and 2860 (s), 1440 and 1380 (m), 1300, 1185, 1090, 1060, 1020, 910, 840, and 790 (s), 450 (sh), 385 (m), 300 (s), 248 (s) cm^{-1}; IR (bis(THF) adduct) 2980–2840 (s), 1435 (m), 1375 (m), 1050 (s), 900 (s), 385 (m, br), 305 (s), 240 (s) cm^{-1}; ^1H NMR (THF-d_8) *J* = +172 Hz, $W_{1/2}$ = 24 Hz; ^1H NMR (toluene-d_8) *J* = +266 Hz, $W_{1/2}$ = 36 Hz; hydrolysis % C_5Me_5 calcd 40.4, found 41.0. Anal. Calcd for [C$_{28}$H$_{50}$Cl$_2$LiO$_2$Yb]: C, 50.23; H, 7.53; Cl, 10.59; Yb, 26.19. Found: C, 50.12; H, 7.43; Cl, 10.99; Yb, 26.36.

Li[YbCl$_2$(C$_5$Me5)$_2$]. (a) Li[YbCl$_2$(C$_5$Me$_5$)$_2$](ether)$_2$ as a solid was heated under vacuum at 180 °C until the dark purple changed to gray-green (5–10 min). (b) Finely powdered Li[YbCl$_2$(C$_5$Me$_5$)$_2$](ether)$_2$ was stirred vigorously in hexane or toluene at 20 °C until the color of the suspended solids was green (<1 h). The green product (95% yield) was collected by filtration and dried in vacuum: IR 2960, 2900, and 2860 (s), 1430 (m), 1380 (m), 1060 (w), 1020 (s), 800 (m), 720 (m), 460 (m, br), 380 (m, br), 300 (s), 240 (m) cm^{-1}. Calcd for [C$_{20}$H$_{30}$Cl$_2$LiYb]: C, 46.08; H, 5.80; Cl, 13.60; Yb, 33.19. Found: C, 49.17; H, 6.19; Cl, 13.75; Yb, 32.63.

Li[LuCl$_2$(C$_5$Me$_5$)$_2$](ether)$_2$ (5). A mixture of LuCl$_3$ (2.8 g, 0.01 mol) and LiC$_5$Me$_5$ (2.8 g, 0.02 mol) in THF (100 mL) was refluxed for 3 h. The solution was evaporated to complete dryness, and residues were extracted with ether (200 mL) overnight. Extracts were filtered, and the filtrate was concentrated to ~30 mL. The precipitated product was collected by filtration and dried briefly under vacuum: yield of white powder 2.7 g (40%); IR (2800–2990 (s), 1440 (s), 1380 (s), 1300 (m), 1185 (m), 1095 (s), 1065 (s), 1025 (s), 915 (m), 840 (m), 795 (m), 495 (m), 370 (m), 290 (m), 242 (m) cm^{-1}; ^1H NMR (acetone-d_6 or THF-d_8) δ 1.2 (t, 4CH$_3$), 1.96 (s, 10 CH$_3$), 3.4 (q, 4 CH$_2$); ^{13}C NMR (THF-d_8) δ 11.63 (C$_5$Me$_5$) and 114.97 (C$_5$Me$_5$). Anal. Calcd for [C$_{28}$H$_{50}$Cl$_2$LiLuO$_2$]: C, 50.08; H, 7.51; Cl, 10.56; Lu, 26.0. Found: C, 49.97; H, 7.55; Cl, 10.83; Lu, 26.50.

Li[LuCl$_3$(C$_5$Me$_5$)](ether). This complex was sometimes isolated from the supernatent liquor after precipitation of 5 from concentrated ether solution: ^1H NMR (THF-d_8) δ 2.03. Anal. Calcd for [C$_{14}$H$_{25}$Cl$_3$LiLuO]: C, 33.79; H, 5.06; Cl, 21.37; Li, 1.39; Lu, 35.16; O, 3.22. Found: C, 33.72; H, 4.84; Cl, 21.70; Li, 1.66; Lu, 36.13; O, 3.60.

(19) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1–5.
(20) For synthesis and properties of the parent compound C$_5$H$_5$I, see: Breslow, R.; Hoffman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 2110–2111. Breslow, R.; Hoffman, J. M.; Perchonock, C. *Tetrahedron Lett.* **1973**, 3723–3726.

(21) Jutzi P.; Kohl, F. *J. Organomet. Chem.* **1979**, *164*, 141.

Li[YbCl$_2$(C$_5$H$_4$SiCH$_3$Ph$_2$)$_2$](ether)$_2$ (6) (Ph = C$_6$H$_5$). A solution of LiC$_5$H$_4$SiCH$_3$Ph$_2$ (1.08 g, 0.004 mol) was stirred with YbCl$_3$ for 2 days at 20 °C. The solution was filtered, and the filtrate was evaporated to dryness. Residues were taken up in ether (30 mL) and the solution was cooled to –40 °C. The product was obtained pure as orange crystals: 0.9 g (50%); ether dissociated on standing at 20 °C for several days or when stirred with solvents such as pentane; the ether-free material was white; VIS (ether) 360 nm (235); VIS (THF) 370 nm; IR 3060, 3040 (m), 2830–3000 (s), 1440 and 1370 (m), 1250, 1175, 1110, 1080, 1060, and 1040 (s), 995, 970, 950, 895, 865, and 850 (m), 500 (m), 470, 435, 240 (w) cm^{-1}. Anal. Calcd for [C$_{44}$H$_{54}$Cl$_2$LiO$_2$Si$_2$Yb]: C, 57.32; H, 5.90. Found: C, 57.26; H, 5.92.

Li[LuCl$_2$(C$_5$H$_4$SiCH$_3$Ph$_2$)$_2$] (7). This white complex was isolated in 80% yield by a procedure analogous to that described for ytterbium. After the complex was dried under vacuum at 20 °C, no ether of solvation was present: ^{1}H NMR (THF-d_8) δ 0.92 (s, 3 H, CH$_3$), 5.58 and 5.91 (t, each 2 H, J_{HH} = 3Hz), 7.28 (m, 6 H), 7.49 (m, 4 H). Anal. Calcd for [C$_{36}$H$_{34}$Cl$_2$LiLuSi$_2$]: C, 55.74; H, 4.42; Cl, 9.14; Lu, 22.56. Found: C, 55.16; H, 4.67; Cl, 9.48; Lu, 22.95 (this analysis shows the presence of 6% LuCl$_2$(C$_5$H$_4$SiCH$_3$Ph$_2$) and 94% 7).

Yb(C$_5$Me$_5$)$_2$AlCl$_4$ (8). A suspension of green Li[YbCl$_2$(C$_5$Me$_5$)$_2$], (1.0 g, 0.0019 mol), unsolvated, and AlCl$_3$ (0.22 g, 0.0017 mol) was stirred in pentane (50 mL) at 20 °C for 8 h. The blue solution was filtered, and the filtrate was maintained at –40 °C until deep blue crystals formed. Crystals were collected by filtration and dried: first crop 0.57 g, 55%. At 175 °C the compound underwent a partial melt, with color change to teal blue, and at 200 °C it underwent a further color change to light green: VIS (pentane) 620 (273), 883 (35), 912 (45), 928 (33), 970 (106), 986 (66), and 997 (61) nm; λ_{max} 706 (toluene); IR 2980 (s), 2920 (s), 2860 (s), 1585 (w), 1435 (m), 1380 (m), 1260 (w), 1060 (w), 1025 (s), 840 (w), 800 (w), 720 (w), 545 (s), 495 (s), 410 (s), 315 (s), 215 (m) cm^{-1}; ^{1}H NMR (toluene-d_8) J = +939.6 Hz, $W_{1/2}$ = 66 Hz; ^{1}H NMR (CDCl$_2$) J = +948.6 Hz, $W_{1/2}$ = 50 Hz. Anal. Calcd for [C$_{20}$H$_{30}$AlCl$_4$Yb]: C, 39.23; H, 4.93; Cl, 23.16; Yb, 28.26. Found: C, 39.47; H, 5.14; Cl, 22.97; Yb, 28.01.

Lu(C$_5$Me$_5$)AlCl$_4$. This white complex was prepared by a procedure directly analogous to that described for the ytterbium complex 8. From Li[LuCl$_2$(C$_5$Me$_5$)$_2$] (1 g) was obtained 1.5 g of Lu(C$_5$Me$_5$)$_2$AlCl$_4$ (82%): ^{1}H NMR (toluene-d_8) δ 2.06.

Anal. Calcd for [C$_{20}$H$_{30}$AlCl$_4$Lu]: C, 39.10; H, 4.92; Al, 4.39; Cl, 23.08; Lu, 28.48. Found: C, 38.92; H, 4.90; Al, 4.51; Cl, 23.41; Lu, 28.67.

YbCl(C$_5$Me$_5$)$_2$(THF). To a solution of Yb(C$_5$Me$_5$)$_2$AlCl$_4$ (0.7 g, 0.00115 mol) in toluene (20 mL) was added THF (0.5 mL). The color changed from blue to purple immediately. The solution was cooled to –40 °C until purple crystals formed. The crystals were collected by filtration: 0.28 g, mp 229–230 °C. The filtrate was cooled again and a second crop, 0.2 g (overall 87%), was collected: mp 229–230 °C; VIS (THF) 505 (255), 880 (19), 903 (32), 917 (32), 960 (80) nm; IR 2860–3000(s), 1440 (m), 1380 (m), 1020 (s), 870 (s), 380 (m), 300 (s), 250 (m); ^{1}H NMR (THF-d_8) J = +130 Hz, $W_{1/2}$ = 64 Hz; ^{1}H NMR (toluene-d_8) J = +117 Hz, $W_{1/2}$ = 64 Hz. Anal. Calcd for [C$_{24}$H$_{38}$ClOYb]: C, 52.31; H, 6.95; Cl, 6.43; Yb, 31.40. Found: C, 51.85; H, 6.89; Cl, 6.95; Yb, 31.02.

Collection and Reduction of X-ray Intensity Data. Crystals of the four compounds were sealed in glass capillaries under nitrogen and mounted on a Syntex P3 diffractometer. The crystal system, space group, and approximate unit cell dimensions of each crystal were determined during a preliminary investigation. The unit cell dimensions were subsequently refined from the Bragg angles of 50 computer-centered reflections. A summary of the crystal data is given in Table I.

Intensity data were collected using the ω-scan technique with background measurements at both ends of the scan (total background time was equal to the scan time). The intensities of four standard reflections were monitored periodically; only statistical fluctuations were noted. The intensities of several reflections were measured in 10° increments about the diffraction vector; as a result, empirical corrections for absorption were applied.

The solution and refinement of the structure were carried out on a PDP-11 computer using local modifications of the programs supplied by the Enraf-Nonius Corp.[22] The atomic scattering factors were taken
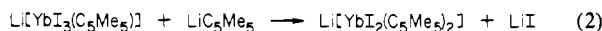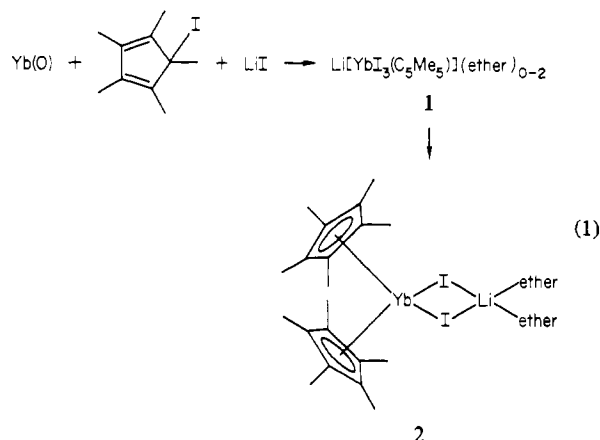
from the tabulations of Cromer and Waber;[23] anomalous dispersion corrections were by Cromer. In the least-squares refinement, the function minimized was $[\sum w|F_o| - |F_c|]^2$ with the weights, w, assigned as $1/\sigma^2(F_o)$. The standard deviations of the observed structure factors, $\sigma(F_o)$, were based on counting statistics and an "ignorance factor", p, of 0.02.[24]

Structures 4, 6, and 8 were solved by heavy-atom techniques and refined by the full-magrix least-squares method. Structure 2 was solved by MULTAN and refined by the full-matrix least-squares method.

Selected geometric parameters for ytterbium complexes 2, 4, 6, and 8 are given in Table II. One of the carbon atoms in the ether groups in Li[Yb(C$_5$Me$_5$)$_2$I$_2$](ether)$_2$ was found to be disordered; the two positions were labeled C(7) and C(7)P and assigned occupation factors of 0.5.

Results and Discussion

Iodopentamethylcyclopentadiene (C$_5$Me$_5$I) reacts with ytterbium metal and lithium iodide in ether to give, sequentially, the two trivalent complexes 1 and 2, as shown in eq 1 and 2.

$$\text{Yb(0)} + \text{C}_5\text{Me}_5\text{I} + \text{LiI} \longrightarrow \text{Li[YbI}_3(\text{C}_5\text{Me}_5)\text{I](ether)}_{0-2}$$

1

$$ \tag{1}$$

2

$$\text{Li[YbI}_3(\text{C}_5\text{Me}_5)\text{]} + \text{LiC}_5\text{Me}_5 \longrightarrow \text{Li[YbI}_2(\text{C}_5\text{Me}_5)_2\text{]} + \text{LiI} \tag{2}$$
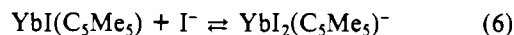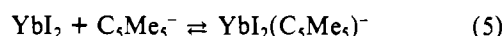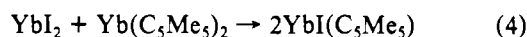
Oxidation of ytterbium metal to the trivalent complexes 1 and 2 probably proceeds through initial formation of divalent ytterbium complexes such as YbI(C$_5$Me$_5$) (eq 3). Evans[13]

$$\text{Yb(0)} + \text{C}_5\text{Me}_5\text{I} \rightarrow \text{Yb}^{II}\text{I(C}_5\text{Me}_5) \tag{3}$$
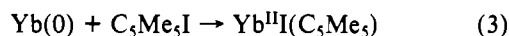
has reported the reactions of a number of aryl and alkyl iodides with ytterbium metal to form "Grignard-like" ytterbium(II) reagents analogous to the reaction in eq 3.

Observation of YbI(C$_5$Me$_5$) or Li[YbI$_2$(C$_5$Me$_5$)] in our system is prevented by the rapid production of paramagnetic species. However, since it is possible to generate both YbI-(C$_5$Me$_5$) and Li[YbI$_2$(C$_5$Me$_5$)] by independent routes[25] (shown in eq 4 and eq 5 with Li$^+$ as counterion), the one-electron

$$\text{YbI}_2 + \text{Yb(C}_5\text{Me}_5)_2 \rightarrow 2\text{YbI(C}_5\text{Me}_5) \tag{4}$$

$$\text{YbI}_2 + \text{C}_5\text{Me}_5^- \rightleftharpoons \text{YbI}_2(\text{C}_5\text{Me}_5)^- \tag{5}$$

$$\text{YbI(C}_5\text{Me}_5) + \text{I}^- \rightleftharpoons \text{YbI}_2(\text{C}_5\text{Me}_5)^- \tag{6}$$
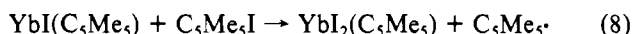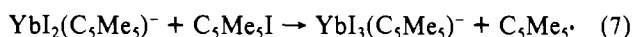
oxidations of these complexes were examined. The two complexes can interconvert (eq 6) but neither is appreciably soluble, as an ether solvate, in ether. Addition of LiI in ether to a solution of the THF solvate of YbI(C$_5$Me$_5$) in ether resulted in precipitation of Li[YbI$_2$(C$_5$Me$_5$)], suggesting that this may be the predominate form of organometallic divalent ytterbium under the reaction conditions described for eq 1. (In the more coordinating solvent, THF, the equilibrium

(22) Frenz, B. A. In *Comput. Crystallog., Proc. Int. Summer Sch.* **1978**, 64–71.

(23) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) Table 2.2B; (b) Table 2.3.1.
(24) Corfield, B. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.
(25) Watson, P. L., unpublished results.

greatly favors $YbI(C_5Me_5)$ (δ 2.01) over $Li[YbI_2(C_5Me_5)]$ (δ 1.90), both species being fairly soluble). Suspensions of Li-$[YbI_2(C_5Me_5)]$ react over several hours with C_5Me_5I in ether, as shown in eq 7. The isolated green product is shown to be

$$YbI_2(C_5Me_5)^- + C_5Me_5I \rightarrow YbI_3(C_5Me_5)^- + C_5Me_5\cdot \quad (7)$$

$$YbI(C_5Me_5) + C_5Me_5I \rightarrow YbI_2(C_5Me_5) + C_5Me_5\cdot \quad (8)$$

1 by elemental analysis and visible–near-IR spectroscopy. This reaction may occur via either the anionic or the neutral divalent species. Ethereal suspensions of $YbI(C_5Me_5)$ are in fact oxidized by C_5Me_5I to blue $YbI_2(C_5Me_5)$ within a 0.5 h (eq 8). Subsequent addition of LiI immediately generates **1**. In THF the oxidation of $Li[YbI_2(C_5Me_5)]$ by C_5Me_5I is more rapid than in ether. The intermediate **1** is not observed in THF although **2** is the final product.

As well as undergoing oxidation, $Li[YbI_2(C_5Me_5)]$ also mediates the metahetical transformation of **1** to **2**, with YbI_2 as the observed byproduct. Equations 5 and 9 describe this reaction.

$$YbI_3(C_5Me_5)^- + YbI_2(C_5Me_5)^- \rightarrow$$
$$YbI_2(C_5Me_5)_2^- + YbI_2 + I^- \quad (9)$$
$$\mathbf{2}$$
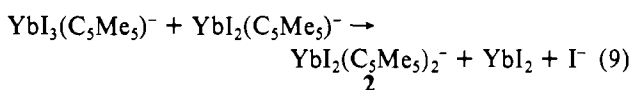
The above observations are consistent with the following proposal. The formation of **1** and **2** from ytterbium metal occurs in three steps: (1) oxidation of ytterbium metal to $Yb^{II}I(C_5Me_5)$, probably followed by complexation of LiI to give $Li[YbI_2(C_5Me_5)]$ (2) oxidation of the divalent species to the trivalent complex **1**, and (3) reaction of **1** with LiC_5Me_5 (or donor complex thereof such as $Li[YbI_2(C_5Me_5)]$) to give **2**. It is important to note that the reaction of ytterbium metal with C_5Me_5I does not yield organometallic species in the absence of LiI. Ytterbium metal and C_5Me_5I alone (equimolar in ether) give the dimer $C_{10}Me_{10}$ and YbI_3 as products. (On further standing, YbI_3 is reduced back to YbI_2 by the remaining ytterbium metal.) This reaction proceeds through a grey-green color which may indicate some intermediate ytterbium(III) organometallic species. The exact role played by iodide ion in promoting the organometallic product **1** is not clear. That both the di- and trivalent complexes are stabilized in ether as anions is apparent. It was considered that halide ion may also catalyze the oxidation of the divalent complex, as has been noted for SmI_2[26] reactions with alkyl tosylates, but since both the neutral and anionic divalent complexes are oxidized rapidly by C_5Me_5I on the time scale of the reaction with ytterbium metal, such an effect would not account for the product difference. Back-reduction of the trivalent complexes $YbI_2(C_5Me_5)$ and **1** by ytterbium metal is not dramatically affected by the presence of lithium iodide. For example, the concentration of $YbI_2(C_5Me_5)$ (approximately 0.002 M in ether) is diminished in the presence of excess ytterbium metal by 30% after 36 h (with formation of YbI_2) in the absence of lithium iodide. With 2–3 equiv of lithium iodide only a slight difference in the rate of reduction occurs (20–25% depletion of **1** after 36 h). Another possibility, the effect of iodide on the initial oxidation (eq 3), remains unassessed since this step could not be studied independently.

Substitution Reactions of MCl₃ (M = Yb, Lu). **(a)** Li-$[MCl_3(C_5Me_5)]$ and $Li[MCl_2(C_5Me_5)_2]$ **(M = Yb, Lu).** Substitution reactions of MCl_3 with LiC_5Me_5 proceed by sequential formation of the very stable anionic complexes Li-$[MCl_3(C_5Me_5)]$ and $Li[MCl_2(C_5Me_5)_2]$, which are chloro analogues of **1** and **2**. The neutral complexes $YbCl_2(C_5Me_5)$ and $YbCl(C_5Me_5)_2$ are isolated from the reaction mixtures on occasion, but both are minor products under the reaction
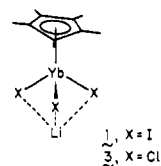

Figure 1. Generalized structure of $Li[MX_3(Cp)]$ complexes.

conditions used. Although formulae shown above for the various complexes do not specifically include associated ether ligands (diethyl ether or THF), complexes are in fact always obtained as etherates. For anionic complexes, where the lithium is solvated rather than the heavy metal, the ether is somewhat labile at 20 °C, and complexes are often isolated containing nonstoichiometric amounts of ether. The stoichiometric complexes $Li[YbCl_3(C_5Me_5)](THF)$ and Li-$[MCl_2(C_5Me_5)_2](ether)_2$ were carefully isolated for purposes of complete characterization.

Blue $Li[YbCl_3(C_5Me_5)]$ **(3)** is obtained in high yield by reaction of equimolar amounts of LiC_5Me_5 and anhydrous $YbCl_3$ in THF (eq 10). When the LiC_5Me_5 is not finely

$$YbCl_3 + LiC_5Me_5 \rightarrow Li[YbCl_3(C_5Me_5)] \quad (10)$$
$$\mathbf{3}$$

powdered, **3** is not observed since further reaction of the THF-soluble **3** with LiC_5Me_5 to form **4** (eq 11) is then kinetically competitive with the initial reaction. Although the

$$Li[YbCl_3(C_5Me_5)] + LiC_5Me_5 \rightarrow$$
$$Li[YbCl_2(C_5Me_5)_2] + LiCl \quad (11)$$
$$\mathbf{4}$$

netically competitive with the initial reaction. Although the molecular structure of this complex has not been determined by X-ray crystallography, it may be similar to the structure of $[LiCr(C_5H_5)Cl_3(THF)_2](DME)$ determined by Muller and Krausse.[27] This generalized structure, postulated for **1** and **3**, is depicted in Figure 1.

Addition of 2 equiv of LiC_5Me_5 to $YbCl_3$ gives purple Li-$[YbCl_2(C_5Me_5)_2]$ **(4)** in a mildly exothermic reaction. As mentioned above, addition of 1 equiv of LiC_5Me_5 to **3** in THF also gives **4**. The THF adduct $Li[YbCl_2(C_5Me_5)_2](THF)_n$ **(4a)** is soluble in toluene. By ^1H NMR and elemental analysis, n varies between 2 and 3. With $n = 2$ the structure is probably analogous to that of the diethyl ether complex (vide infra), whereas a structure with lithium coordinated to three THF oxygens and only one of the two ytterbium-bound chlorines is most likely when $n = 3$. The bis(diethyl ether) complex $Li[YbCl_2(C_5Me_5)_2](ether)_2$ **(4b)** (obtained by recrystallization of the THF adduct from ether at low temperature) is not soluble in toluene and is much less soluble in ether than **4a**. Ether was readily removed from **4b** either by heating the complex under vacuum or by simply stirring the complex in toluene or pentane. Unsolvated **4** is a green solid, insoluble in all noncoordinating solvents, but readily soluble in ethers (regenerating complexes such as **4a** and **4b**) and CH_3CN.

The white lutetium complex $Li[LuCl_2(C_5Me_5)_2]$ **(5)** is also prepared by addition of LiC_5Me_5 to $LuCl_3$. Isolation and solubility properties of the THF and ether adducts are similar to those of the ytterbium system just described. When only 1 equiv of LiC_5Me_5 is used, the usual products are **5** and the white, THF-soluble $LuCl_3THF_{3,4}$ (each in approximately 50% yield). Occasionally the trichloride $Li[LuCl_3(C_5Me_5)]$ is isolated from the most ether soluble fractions of the crude reaction products.

(b) $Li[MCl_2(C_5H_4SiCH_3Ph_2)_2]$ **(M = Yb, Lu).** The ready isolation of $Li[MCl_2(C_5H_4SiCH_3Ph_2)_2]$ **(6, M = Yb; 7, M = Lu)** (as diethyl ether adducts) from MCl_3 and $LiC_5H_4SiCH_3Ph_2$ demonstrates that steric congestion of lig-

(26) Girard, P.; Namy, J. L.; Kagan, H. B.; *J. Am. Chem. Soc.* **1980**, *102*, 2693–2698; *Nouv. J. Chim.* **1977**, *1*, 5.

(27) Müller, B.; Krausse, J. *J. Organomet. Chem.* **1972**, *44*, 141–159.
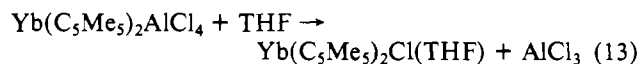
Table I

	2	4	6	8
		(a) Crystal Data		
formula	$C_{28}H_{50}LiI_2O_2Yb$	$C_{28}H_{50}Cl_2LiO_2Yb$	$C_{44}H_{54}Cl_2LiO_2Si_2Yb$	$C_{20}H_{30}AlCl_4Yb$
fw	852.50	66.9.60	921.98	612.30
crystal system	tetragonal	monoclinic	triclinic	monoclinic
space group	$P\bar{4}2_1m$	$C2/c$	$P\bar{1}$	$P2_1/n$
		(b) Unit Cell Parameters (Mo Kα radiation, λ = 0.710 69 Å, −100 °C)		
a, Å	11.257 (2)	16.170 (2)	14.053 (2)	18.184 (3)
b, Å		13.774 (2)	15.495 (3)	12.923 (2)
c, Å	13.068 (13)	13.998 (2)	10.423 (3)	10.364 (2)
α, deg			98.85 (3)	
β, deg		90.91 (1)	101.03 (1)	
γ, deg			88.33 (1)	
V, Å³	1656	3117	2201	2364.5
Z	2	4	2	4
D_x, g cm⁻³	1.710	1.427	1.391	1.720
		(c) Data Collected on a Syntex P3 Diffractometer (ω scans, 4 < 2θ < 55°)		
cryst dimens, mm	0.26 × 0.25 × 0.40	0.26 × 0.28 × 0.46	0.36 × 0.27 × 0.41	0.20 × 0.16 × 0.29
scan range, (deg)	1.0	1.0	1.2°	1.0
reflctns measd	2239	5199	10146	5443
transmission factors	0.88–0.98	0.83–1.00	0.81–1.00	0.85–1.00
		(d) Full-Matrix Least-Squares Refinement		
anisotropic thermal parameter	Yb, I	Yb, Cl, O, C, Li	Yb, Cl, Si	C, Al, Cl, Yb
isotropic thermal parameters	O, C, Li		O, C, Li	
hydrogens atoms	not included	not included	not included	not included
variables	50	155	234	235
reflections refined	1116	3378	8051	4525
$I = n(I)$, n	2	2	6	2
$R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$	0.038	0.025	0.036	0.026
largest peak in final				0.38
difference Fourier map, e Å⁻³	0.73, near heavy atom and hydrogens	0.60, hydrogen atoms	0.68, near far end of phenyl groups	0.38, hydrogens

ands is not a prerequisite for formation of the $Li[MX_2Cp'_2]$ systems.

Examination of the molecular structure of **6** (vide infra) shows substantially less steric bulk above and below the YbX_2Li plane than in the structures of **2** and **4** (vide infra) and probably no more than in the dimer $[Yb(C_5H_4CH_3)_2$-$Cl]_2$.[31] Thus it may be reasonably inferred that substitution reactions of these lanthanide halides generally proceed by a series of addition–elimination steps with anionic addition complexes as stable intermediates or the kinetic products. Long reaction times or extraction with nonpolar solvents may favor isolation of the neutral dimers, $[MCp'_2X]_2$, commonly observed with less hindered ligand systems. Lappert et al.[28] have also noted this possibility, in connection with the isolation of both $M(CH_2SiMe_3)_3(THF)_2$ and $Li(THF)_4[MCl(CH)$-$SiMe_3)_2)_3]$ (M = Er, Yb). In addition, a yttrium complex similar to **6** and **7**, $Li(THF)_2[Y(C_5H_4SiMe_3)_2Cl_2]$, was prepared by these workers. With sterically hindered ligands, the anionic complexes may be the thermodynamic as well as kinetic products.

Reactivity of $M'[YbCl_2(C_5Me_5)_2]$ (M' = Li, K). (a) With Lewis Acid. In an attempt to prepare the decamethylytterbicinium cation, ether-free $Li[Yb(C_5Me_5)_2Cl_2]$ was treated with $AlCl_3$ in pentane. The blue product **8** (eq 12)

$$Li[YbCl_2(C_5Me_5)_2] + AlCl_3 \rightarrow \underset{\mathbf{8}}{Yb(C_5Me_5)_2AlCl_4} + LiCl$$
$$(12)$$

$$Yb(C_5Me_5)_2AlCl_4 + THF \rightarrow$$
$$Yb(C_5Me_5)_2Cl(THF) + AlCl_3 \quad (13)$$

was shown by X-ray diffraction analysis (vide infra) to contain a coordinated $AlCl_4$ ion. The lutetium analogue of **8** is pre-

(28) Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Holton, J.; McMeeking, J.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1978**, 140–142.
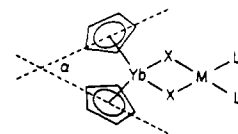
Figure 2. Generalized structure of $Cp_2MX_2M'L_2$.

pared in the same fashion. Reaction of **8** with THF does not promote ionic dissociation. Instead, the neutral monochloride complex is obtained (eq 13). The desired trivalent cation $Yb(C_5Me_5)_2^+$ is, however, readily prepared as the PF_6^- salt by oxidation of the divalent species $Yb(C_5Me_5)_2$[6,25] with Fe-$(C_5H_5)_2PF_6$.

(b) Reduction. The potassium salt $K[YbCl_2(C_5Me_5)_2]$ (prepared in situ from $YbCl_3$ and 2 equiv of KC_5Me_5) is reduced to the divalent complexes $Yb(C_5Me_5)_2DME$ and $Yb(C_5Me_5)_2(CH_3CN)_{1,2}$[6,25] with 1% Na/Hg in DME and CH_3CN, respectively. Direct metathesis reactions with ytterbium(II) halides give these products in better yield. The reduction of $K[YbCl_2(C_5Me_5)_2]$ in THF was even less effective than in glyme, suggesting that the stability of the solvated $Yb(C_5Me_5)_2L_2$ may contribute significantly to the reduction potential. A study of the electrochemical properties of these and related Yb(II)/Yb(III) couples is in progress.

Structures of 2, 4, 6 and 8. Molecular structures of the four ytterbium complexes **2, 4, 6,** and **8** were determined by X-ray crystallography in order to differentiate among possible bonding modes in these paramagnetic (f^{13}) systems.

The orange complex $Li[YbCl_2(C_5H_4SiCH_3Ph_2)_2](ether)_2$ (**6**) was obtained as triclinic crystals from ether solution at −40 °C. Purple crystals of $Li[YbCl_2(C_5Me_5)_2](ether)_2$ (**4**) were similarly grown from ether, while blue $Yb(C_5Me_5)_2AlCl_4$ (**8**) was crystallized from pentane. Both **4** and **8** gave crystals with monoclinic symmetry. The diiodide complex $Li[YbI_2$-$(C_5Me_5)_2](ether)_2$ (**2**) was crystallized from ether solution at −40 °C; the deep purple crystals belonged to the tetragonal

Table II. Pertinent Geometric Parameters for Li[YbI$_2$(C$_5$Me$_5$)$_2$](ether)$_2$ (2),[a] Li[YbCl$_2$(C$_5$Me$_5$)$_2$](ether)$_2$ (4),[b] Li[YbCl$_2$(C$_5$H$_4$SiCH$_3$Ph$_2$)$_2$](ether)$_2$ (6),[c] and Yb(C$_5$Me$_5$)$_2$AlCl$_4$ (8)[d]

(a) Selected Bond Distances (Å) with Estimated Standard Deviations

2		4		6		8	
Yb–I	3.027 (1)	Yb–Cl(1)	2.596 (1)	Yb–Cl	2.593 (1)	Yb–Cl(1)	2.760 (1)
		Yb–Cl(2)	2.594 (1)			Yb–Cl(2)	2.752 (1)
Yb···Li	4.119 (12)	Yb···Li	3.478 (6)	Yb···Li	3.506 (6)	Yb···Al	3.65
Yb–C(1)	2.625 (10)	Yb–C(1)	2.603 (3)	Yb–C(1)	2.638 (2)	Yb–C(1)	2.559 (3)
Yb–C(2)	2.620 (8)	Yb–C(2)	2.594 (3)	Yb–C(2)	2.621 (2)	Yb–C(2)	2.572 (3)
Yb–C(3)	2.629 (8)	Yb–C(3)	2.599 (3)	Yb–C(3)	2.636 (2)	Yb–C(3)	2.586 (3)
		Yb–C(4)	2.630 (3)	Yb–C(4)	2.628 (2)	Yb–C(4)	2.601 (3)
		Yb–C(5)	2.619 (3)	Yb–C(5)	2.647 (2)	Yb–C(5)	2.585 (3)
		Yb–C(19)	2.622 (3)			Yb–C(11)	2.609 (3)
		Yb–C(20)	2.607 (3)			Yb–C(12)	2.590 (3)
		Yb–C(21)	2.594 (3)			Yb–C(13)	2.581 (3)
		Yb–C(22)	2.608 (3)			Yb–C(14)	2.559 (3)
		Yb–C(23)	2.631 (3)			Yb–C(15)	2.597 (3)
Li–I	2.812 (15)	Li–Cl(1)	2.390 (6)	Li–Cl	2.390 (4)	Al–Cl(1)	2.187 (1)
		Li–Cl(2)	2.412 (6)			Al–Cl(2)	2.185 (1)
Li–O	1.904 (15)	Li–O(1)	1.924 (7)	Li–O	1.957 (4)	Al–Cl(3)	2.094 (1)
		Li–O(2)	1.935 (7)			Al–Cl(4)	2.097 (1)
C(1)–C(2)	1.427 (10)	C(1)–C(2)	1.428 (4)	C(1)–C(2)	1.415 (3)	C(1)–C(2)	1.411 (5)
C(2)–C(3)	1.426 (10)	C(1)–C(5)	1.430 (4)	C(2)–C(3)	1.413 (3)	C(1)–C(5)	1.424 (5)
C(3)–C(3')	1.312 (16)	C(2)–C(3)	1.402 (4)	C(3)–C(4)	1.437 (3)	C(2)–C(3)	1.424 (5)
		C(3)–C(4)	1.429 (4)	C(4)–C(5)	1.419 (4)	C(3)–C(4)	1.407 (5)
		C(4)–C(5)	1.415 (5)	C(5)–C(1)	1.419 (4)	C(4)–C(5)	1.419 (5)
		C(19)–C(20)	1.435 (4)			C(11)–C(12)	1.421 (5)
		C(19)–C(23)	1.437 (4)			C(11)–C(15)	1.417 (5)
		C(20)–C(21)	1.422 (4)			C(12)–C(13)	1.422 (5)
		C(21)–C(22)	1.421 (5)			C(13)–C(14)	1.421 (5)
						C(14)–C(15)	1.431 (5)
C(1)–C(4)	1.472 (18)	C(1)–C(6)	1.504 (4)	Si(1)–C(1)	1.862 (1)	C(1)–C(6)	1.520 (5)
C(2)–C(5)	1.509 (14)	C(2)–C(7)	1.521 (3)	Si(1)–C(6)	1.884 (4)	C(2)–C(7)	1.529 (5)
C(3)–C(6)	1.507 (15)	C(3)–C(8)	1.520 (4)	Si(1)–C(7)	1.884 (3)	C(3)–C(8)	1.521 (5)
		C(4)–C(9)	1.519 (4)	Si(1)–C(13)	1.871 (3)	C(4)–C(9)	1.524 (5)
		C(5)–C(10)	1.505 (4)	Si(2)–C(19)	1.863 (3)	C(5)–C(10)	1.523 (5)
				Si(2)–C(24)	1.874 (4)	C(11)–C(16)	1.510 (5)
				Si(2)–C(25)	1.875 (3)	C(12)–C(17)	1.523 (5)
				Si(2)–C(31)	1.880 (3)	C(13)–C(18)	1.522 (5)
						C(14)–C(19)	1.515 (5)
						C(15)–C(20)	1.504 (5)
I···I'	4.132 (2)	Cl(1)···Cl(2)	3.534 (1)	Cl(1)···Cl(2)	3.577 (1)	Cl(1)···Cl(2)	3.293 (1)
I···C$_4$	3.850 (5)	Cl(1)···C(6)	3.469 (2)			Cl(1)···C(20)	3.522 (4)
		Cl(2)···C(10)	3.318 (2)			Cl(2)···C(10)	3.451 (4)
						Cl(1)···C(9)	3.321 (4)
						Cl(2)···C(16)	3.370 (4)

(b) Selected Bond Angles (Deg) with Estimated Standard Deviations

2		4		6		8	
I–Yb–I	86.10 (2)	Cl–Yb–Cl	85.95 (2)	Cl(1)–Yb–Cl(2)	87.14 (3)	Cl(1)–Yb–Cl(2)	73.36 (3)
		Yb–Cl–Li	89.3 (1)	Yb–Cl(1)–Li	88.3 (2)	Yb–Cl(1)–Al	94.33 (4)
				Yb–Cl(2)–Li	87.9 (3)	Yb–Cl(2)–Al	94.59 (4)
I–Li–I	94.6 (6)	Cl–Li–Cl	95.4 (2)	Cl(1)–Li–Cl(2)	96.3 (2)	Cl(1)–Al–Cl(2)	97.71 (5)
		Cl–Li–O	111.33 (6)	Cl(1)–Li–O(1)	112.4 (3)	Cl(1)–Al–Cl(3)	111.88 (6)
		Cl–Li–O'	117.70 (6)	Cl(1)–Li–O(2)	112.7 (3)	Cl(1)–Al–Cl(4)	112.14 (6)
				Cl(2)–Li–O(1)	106.7 (3)	Cl(2)–Al–Cl(3)	112.00 (6)
				Cl(2)–Li–O(2)	114.0 (3)	Cl(2)–Al–Cl(4)	110.42 (6)
				O(1)–Li–O(2)	113.4 (3)	Cl(3)–Al–Cl(4)	111.92 (6)

(c) Distances (Å) from Selected Mean Planes[e]

2		4		6		8	
C(1)*	0.006 (16)	C(1)*	-0.001 (4)	C(1)*	0.005 (5)	C(1)*	-0.004 (4)
C(2)*	-0.005 (12)	C(12)*	-0.004 (4)	C(2)*	-0.007 (5)	C(2)*	0.006 (4)
C(3)*	0.002 (13)	C(3)*	0.008 (4)	C(3)*	0.007 (5)	C(3)*	-0.005 (4)
C(2')*	-0.005 (12)	C(4)*	-0.008 (4)	C(4)*	-0.004 (5)	C(4)*	0.003 (4)
C(3')*	0.002 (13)	C(5)*	0.006 (4)	C(5)*	-0.001 (5)	C(5)*	0.001 (4)
C(4)	0.024 (28)	C(6)	0.127 (4)	Si(1)	-0.410 (1)	C(6)	0.065 (4)
C(5)	0.101 (21)	C(7)	0.068 (5)	Yb	2.312 (0)	C(7)	0.318 (5)
C(6)	0.263 (24)	C(8)	0.303 (6)	C(19)*	-0.006 (5)	C(8)	0.163 (5)
C(5')	0.101 (21)	C(9)	0.175 (6)	C(20)*	0.004 (5)	C(9)	0.158 (5)
C(6')	0.263 (24)	C(10)	0.180 (5)	C(21)*	-0.001 (5)	C(10)	0.177 (5)
Yb	-2.337 (0)	Yb	-2.341 (0)	C(22)*	-0.003 (5)	Yb	-2.282 (0)
				C(23)*	0.005 (3)	C(11)*	0.000 (5)
				Si(2)	0.232 (1)	C(12)*	0.007 (5)
				Yb	-2.313 (0)	C(13)*	-0.001 (5)

Table II *(Continued)*

	2		4		6		8	
							C(14)*	0.011 (5)
							C(15)*	−0.006 (5)
							C(16)	−0.140 (6)
							C(17)	−0.148 (6)
							C(18)	−0.316 (5)
							C(19)	−0.067 (6)
							C(20)	−0.190 (6)
							Yb	2.286 (0)
Yb*	0.000 (0)	Yb*	0.000 (0)	Yb*	0.000 (0)	Yb*	−0.006 (0)
I*	0.000 (1)	Li*	0.000 (0)	Cl(1)*	0.000 (1)	Cl(1)*	0.008 (1)
Cl'*	0.000 (1)	Cl*	0.000 (1)	Cl(2)*	0.000 (1)	Cl(2)*	0.008 (1)
Li*	0.000 (0)	Cl'*	0.000 (1)	Li*	0.000 (2)	Al*	−0.009 (1)
				Cl(1)*	0.000 (1)		
				Cl(2)*	0.000 (1)		

(d) Dihedral Angle α (Deg)

2	4	6	8
44.4	43.4	49.6	42.7

a See Figure 3. *b* See Figure 4. *c* See Figure 5. *d* See Figure 6. *e* Atoms with an asterisk designate atoms in the plane.
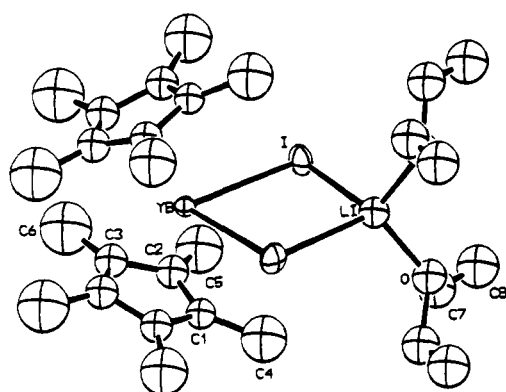
Figure 3. ORTEP drawing of Li[YbI₂(C₅Me₅)₂](ether)₂ (2). The C₅Me₅ rings adopt an eclipsed configuration.
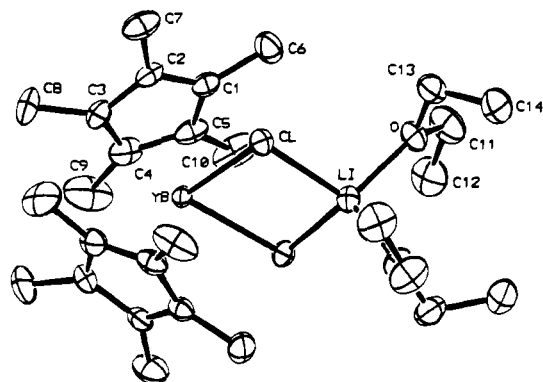

Figure 4. ORTEP drawing of Li[YbCl₂(C₅Me₅)₂](ether)₂ (4) with a crystallographic 2-fold axis of symmetry.
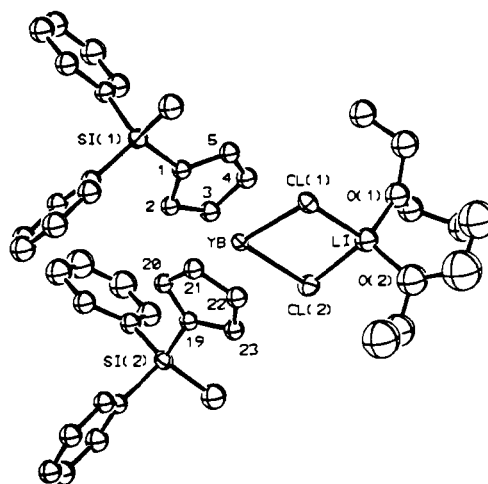
Figure 5. ORTEP drawing of Li[YbCl₂(C₅H₄SiPh₂Me)₂](ether)₂ (6).

system. Further crystal data together with intensity collection and refinement data and results are given in Table I.

The molecular structures of all four complexes conformed to the generalized structure depicted in Figure 2. As mentioned, this structure had been postulated[28] by Lappert for the yttrium complex Li(THF)₂[Y(C₅H₄SiMe₃)₂Cl₂]. Recently a neodymium complex was also suggested[29] to conform to this structure. The molecular structures determined here for the four complexes **2**, **4**, **6**, and **8**, together with that of [(C₅H₅)₂Yb(μ-CH₃)₂Al(CH₃)₂][30] determined previously by Atwood et al. confirm the generality of this structure in organolanthanide chemistry. Each of the complexes, **2**, **4**, **6**, and **8**, exhibits symmetrically distorted tetrahedral coordination around Yb. The center plane normals of the η⁵-cyclopentadienyl rings meet at angles between 135 and 140°, while the X–Yb–X angles are contracted to less than 90°. The same type of distorted tetrahedral coordination exists around the Li or Al atoms. A summary of pertinent geometric data for the four complexes is given in Table II. Ytterbium to ring carbon atom distances (see Table IIa) are reasonably constant (2.559–2.647 Å) in all four structures and are quite comparable with those observed for the related ytterbium species [(C₅H₅)₂Yb(μ-CH₃)₂Al(CH₃)₂],[30] [YbCl(C₅H₄CH₃)₂₃],[31] and

[YbCH₃(C₅H₅)₂]₂.[32] The pendant methyl groups of the η⁵-C₅Me₅ rings in **2**, **4**, and **8** all lie significantly off the C₅ ring planes, toward the outside of the molecules, i.e., on the opposite sides from Yb. As might be expected, the off-plane displacement is greatest for the methyl groups closest to the apex of the dihedral angles α (see Figure 2) formed by in-

(29) Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1980**, *19*, 2190–2191.

(30) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45–53.

(31) Baker, E. C.; Brown, L. D.; Raymond, K. N. *Inorg. Chem.* **1975**, *14*, 1376–1379.

(32) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E.; *J. Chem. Soc., Chem. Commun.* **1976**, 480–481.
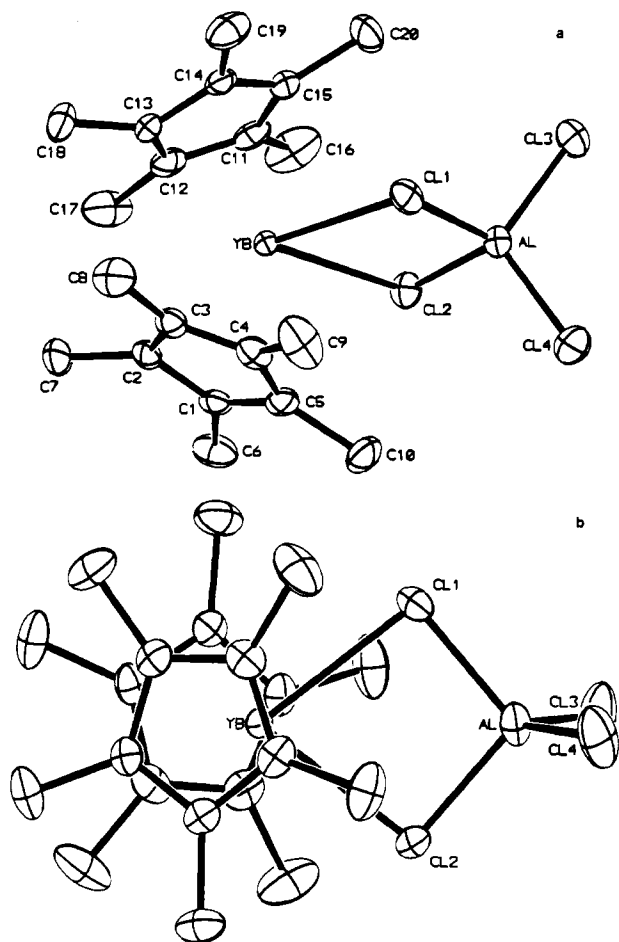
Figure 6. (a) ORTEP drawing of Yb(C$_5$Me$_5$)$_2$AlCl$_4$ (8). (b) View perpendicular to the "YbCl$_2$Al" plane, showing the staggered configuration of the C$_5$Me$_5$ rings.

tersection of the two planes containing the C$_5$ rings. These displacements are given in Table IIc. Presumably these groups encounter the greatest steric interference with their 2-fold rotational equivalents. The silicon atoms Si(1) and Si(2) of 6 are also significantly off the C$_5$ ring planes, by 0.410 (1) and 0.232 (1) Å, respectively.

Similar asymmetric out-of-plane displacements were noted for the methyl groups of (μ-N$_2$)[Zr(C$_5$Me$_5$)$_2$N$_2$]$_2$[33] and TiCl$_2$(C$_5$Me$_5$)$_2$,[34] in which both metal atoms are smaller than Yb (Zr–C$_{av}$ = 2.54 Å and Ti–C$_{av}$ = 2.44 Å) but not for a

complex of the larger thorium atom, bis[μ-(2-butene-2,3-diolato)]-bis[bis(pentamethylcyclopentadienyl)thorium] (Th–C$_{av}$ = 2.84 Å).[35]

In each of the three structures **2**, **4**, and **8**, the atoms YbX$_2$M' (Figure 2) are planar. In **6**, the dihedral angle between the planes defined by YbCl$_2$ and LiCl$_2$ was 6.1°, indicating a slight distortion. Bond lengths and angles pertaining to the YbX$_2$M' units are given in Table IIb. In all cases the angles X–Yb–X were somewhat less than 90°, but the angles X–M'–X were greater than 90°, demonstrating less distorted tetrahedral coordination around M' than around Yb.

The relative orientations of the cyclopentadienyl rings are of interest in these molecules. Viewed normal to the YbX$_2$M' plane, the cyclopentadienyl systems of **4**, **6**, and **8** have similar staggered configurations. (This orientation is illustrated for **8** in Figure 6b.) Neither **4** or **8** showed a perfectly staggered conformation of the rings. The assumption is that nonbonded repulsion between the halide atoms in the coordination plane (i.e., the MX$_2$ plane) and the methyl groups above and below this plane cause deviation from the fully staggered conformation in which ring methyl groups are maximally distant from each other. This steric crowding is illustrated by the observation that the sum of the van der Waals radii for carbon and chlorine atoms (1.70 Å (C) + 1.80 Å (Cl) = 3.50 Å)[36] is at the high end of the range observed (3.32–3.52 Å) for the relevent C···Cl closest contacts. (These distances are shown at the end of Table II.) Replacement of chlorine atoms (van der Waals radius 1.80 Å) in **4** by the larger iodine atoms (van der Waals radius 1.95–2.12 Å[36]) in **2** imposes an even greater steric constraint. The rings in **2** adopt a totally eclipsed configuration with the methyl groups C(4) and C(4') symmetrically disposed above and below the coordination plane and contained in the mirror plane perpendicular to and bisecting the YI$_2$Li unit along the Yb···Li axis. The sum of carbon and iodine atoms, (van der Waals radii (1.70 Å (c) + 2.05 Å (I$_{av}$) = 3.75 Å) compared closely with the observed C(4)···I C distance of 3.85 Å, indicating that nonbonded repulsion would prevent rotation of the rings and adoption of a structure analogous to **4**.

Supplementary Material Available: Final positional parameters (as listings of fractional coordinates, thermal parameters, and structure factor amplitudes (observed and calculated)) (171 pages). Ordering information is given on any current masthead page.

(33) Sanner, R. D.; Manriquez, J. M.; Marsh, R. E.; Bercaw, J. E.; *J. Am. Chem. Soc.* **1976**, *98*, 8351–8357.
(34) McKenzie, T. C.; Sanner, R. D.; Bercaw, J. E.; *J. Organomet. Chem.* **1975**, *102*, 457–466.
(35) Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1978**, *100*, 7112–7114.
(36) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.