Deprotonation of Pentadienyl Dimers: Utilization of Bis(pentadienyl) Groups as Bridging and Chelating Ligands

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The oxidative dimerization of the 2,4-dimethylpentadienyl anion ($2,4$-$C_7H_{11}^-$) leads to 2,4,7,9-tetramethyl-1,3,7,9-decatetraene. A double deprotonation of two methyl groups leads to a bridged bis(pentadienyl) dianion, $K_2[4,4'$-$(CH_2)_2(2$-$C_6H_8)_2]$. This dianion has been found to serve as a useful precursor for bis(pentadienyl)metal complexes. Thus, reaction with a half-equiv of $[Ru(C_5Me_5)Cl]_4$ leads to the expected complex $[4,4'$-$(CH_2)_2(2$-$C_6H_8)_2][Ru(C_5Me_5)]_2$, in which the ligand serves to bridge two metal centers. On the other hand, reaction with YbI_2 in THF leads to a complex, $Yb[4,4'$-$(CH_2)_2(2$-$C_6H_8)_2](THF)_2$, in which the ligand chelates a single metal center. Crystallographic confirmation has been obtained for both of these species. For the former, the space group is $P2_1/c$ with $a = 13.727$ (3) Å, $b = 7.552$ (2) Å, $c = 15.135$ (4) Å, $\beta = 99.54$ (1)°, and $V = 1547.3$ Å^3 for $Z = 2$. For the latter, the space group is $C2/c$ with $a = 13.852$ (2) Å, $b = 10.394$ (1) Å, $c = 16.807$ (3) Å, $\beta = 112.93$ (1)°, and $V = 2228.5$ Å^3 for $Z = 4$. Satisfactory structural refinements were achieved, with respective R (and R_w) values being 0.076 (0.078) and 0.043 (0.050).

Bridged bis(cyclopentadienyl) ligands have been utilized to great advantage in the organometallic chemistry of the transition metals,[1] lanthanides,[2] and actinides.[3] Part of this derives from the fact that these ligands may serve either to chelate a single metal center or to bridge two metals. As it can be expected that analogous bridged bis(pentadienyl) ligands should also prove versatile, we have attempted the synthesis of the requisite dianions and some representative metal complexes. Herein we present some initial results in this area, including demonstrations that these ligands may indeed serve either to chelate a single metal center or serve as a bridge between two metals.

Experimental Section

All hydrocarbon, aromatic, and ethereal solvents were thoroughly dried and deoxygenated by distillation under nitrogen from Na/K benzophenone ketyl immediately before use. Deuterated toluene was degassed over potassium and stored in a glass bulb under nitrogen, while CDCl₃ was dried over P_2O_5 under nitrogen. Infrared mulls were prepared in a glovebox with dry, degassed Nujol.

All operations involving organometallics were carried out under an atmosphere of prepurified nitrogen or in a glovebox. Solvents and solutions were added by glass syringes with stainless steel needles or by a pressure-equalizing addition funnel. Spectroscopic studies were carried out as previously described.[4] Numbers of carbon atoms associated with given ¹³C NMR resonances are reported in accord with their assignments but were not precisely integrated. Analytical data were obtained by Desert Analytics and Oneida Research Labs. $[Ru(C_5Me_5)Cl]_4$, $YbI_2\cdot3THF$, K-$(2,4$-$C_7H_{11})$, and CuCl used in these syntheses were prepared by published procedures.[5-8]

2,4,7,9-Tetramethyl-1,3,7,9-decatetraene, $C_{14}H_{22}$. A 250-mL, 3-neck flask was equipped with a magnetic stirring bar, nitrogen inlet, and pressure-equalizing dropping funnel. The flask was charged with 5.94 g (60.0 mmol) of CuCl and 100 mL of THF. A solution of 6.71 g (50.0 mmol) of potassium 2,4-dimethylpentadienide in 50 mL of THF was prepared in the dropping funnel. The flask was cooled to -78 °C, and the $K(2,4$-$C_7H_{11})$ solution was added to the CuCl slurry dropwise over a period of 15 min. Upon warming, the reaction mixture turned to black. After the reaction mixture had reached room temperature, it was allowed to stir for an additional 6 h. The THF was removed under vacuum, and the residue left was extracted with two 40-mL portions of hexanes. The resulting clear solution was filtered through a Celite pad on a coarse frit. The solvent was removed in vacuo, and 3.88 g (20.4 mmol) of oily product of 2,4,7,9-tetramethyl-1,3,7,9-decatetraene was obtained corresponding to a yield of 81.5% based on $K(2,4$-$C_7H_{11})$.[9]

¹H NMR (CDCl₃, ambient): δ 5.66 (s, 2 H, H3), 4.93 (d, 2 H, $J = 1.5$ Hz, H1), 4.74 (br, 2 H, H1), 2.17 (s, 4 H, H5), 1.82 (s, 6 H, CH_3), 1.81 (s, 6 H, CH_3).

¹³C NMR (CDCl₃, ambient): δ 142.1 (s, C2 or -4), 137.3 (s, C2 or -4), 127.1 (d, $J = 151$ Hz, C3), 113.7 (t, $J = 156$ Hz, C1), 31.7 (t, $J = 127$ Hz, C5), 24.2 (q, $J = 126$ Hz, CH_3), 23.7 (q, $J = 126$ Hz, CH_3).

IR (neat): 3080 (m), 2963 (s), 2934 (s), 2870 (m), 1658 (w, sh), 1638 (m), 1600 (w), 1441 (s), 1372 (m), 1255 (w), 1170 (w), 1068 (w), 1020 (w), 1006 (w), 890 (s), 850 (w, sh), 698 cm⁻¹ (w).

Mass spectrum (EI, 17 eV) [*m/z* (relative intensity)]: 190 (4), 175 (34), 135 (10), 133 (12), 122 (21), 121 (25), 119 (20), 108 (15), 107 (16), 95 (100), 94 (14), 93 (12), 79 (18), 85 (19), 83 (26), 79 (18), 77 (14), 67 (49), 55 (28).

Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.47; H, 11.77.

Potassium Salt of the Bridged Bis(pentadienyl) Dianion, $K_2[4,4'$-$(CH_2)_2(2$-$C_6H_8)_2]$. To a flask containing 3.89 g (34.6 mmol) of potassium *t*-butoxide as a slurry in 40 mL of hexanes was added

(1) (a) Lang, H.; Seyferth, D. *Organometallics* 1991, *10*, 347 and references therein. (b) Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Dong, S.; Chien, J. C. W. *J. Am. Chem. Soc.* 1990, *112*, 2030.

(2) (a) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* 1985, *107*, 8103. (b) John, J.; Tsutsui, M. *J. Coord. Chem.* 1980, *10*, 177. (c) Yan, P.; Hu, N.; Jin, Z.; Chen, W. *J. Organomet. Chem.* 1990, *391*, 313. (d) Qiao, K.; Fischer, R. D.; Paolucci, G.; Traldi, P.; Celon, E. *Organometallics* 1990, *9*, 1361.

(3) (a) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* 1988, *7*, 1828. (b) Secaur, C. A.; Day, V. W.; Ernst, R. D.; Kennelly, W. J.; Marks, T. J. *J. Am. Chem. Soc.* 1976, *98*, 3713.

(4) Newbound, T. D.; Stahl, L.; Ziegler, M. L.; Ernst, R. D. *Organometallics* 1990, *9*, 2962.

(5) (a) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* 1989, *111*, 1698. (b) Koelle, U.; Kossakowski, J. *J. Organomet. Chem.* 1989, *362*, 383.

(6) (a) $YbI_2(THF)_n$ complexes have been described as having n values of 1.5-4, depending in part on the methods of preparation.[6b-d] Our value of n is estimated from the weight of product isolated. (b) Deacon, G. B.; Koplick, A. J. *Inorg. Nucl. Chem. Lett.* 1979, *15*, 263. (c) Watson, P. L. *J. Chem. Soc., Chem. Commun.* 1980, 652. (d) Suleimanov, G. Z.; Rybakova, L. F.; Nuriev, Ya. A.; Kurbanov, T.Kh.; Beletskaya, I. P. *Izv. Akad. Nauk. SSSR* 1983, *32*, 190.

(7) Wilson, D. R.; Stahl, L.; Ernst, R. D. *Organomet. Synth.* 1986, *3*, 136.

(8) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* 1946, *2*, 1.

(9) NMR spectroscopy indicates that an end-center-coupled pentadienyl dimer is present to the extent of ca. 20%. While the doubly deprotonated form of this tetraene is presumably also present to a similar extent in the potassium salt, this has not seemed to complicate the subsequent utilization of this reagent.

15.3 mL (38.1 mmol) of a 2.50 M butyllithium solution in hexanes, at a temperature below -30 °C. After the mixture was warmed to room temperature, a solution of 3.30 g (17.3 mmol) of 2,4,7,9-tetramethyl-1,3,7,9-decatetraene in 20 mL of hexanes was added to the flask dropwise via a pressure-equalizing dropping funnel. The reaction mixture was allowed to stir at room temperature for 2 h, during which time the potassium salt of the bridged bis(pentadienyl) dianion precipitated as a dark red powder. The product was collected on a frit and washed with two 20-mL portions of pentane. Upon being dried in vacuo, 3.52 g (13.2 mmol) of the title compound was obtained (75% yield based on the decatetraene).

[4,4'-(CH₂)₂(2-C₆H₈)₂][Ru(C₅Me₅)]₂. An orange-brown solution of [Cp*RuCl]₄ (0.55 g; 0.5 mmol) in 50 mL of THF was cooled to -78 °C with stirring under nitrogen atmosphere. To this was added dropwise a dark red slurry of the potassium salt of the bridged bis(pentadienyl) dianion (0.41 g; 1.5 mmol) in 30 mL of THF. The reaction mixture was warmed slowly to room temperature and kept stirring over night. After removal of the solvent in vacuo, the dark brown solid left was extracted with two 50-mL portions of a 50% toluene–50% hexanes mixture. The combined extracts were filtered through a Celite pad on a frit, and the yellow-brown filtrate was concentrated to ca. 10 mL before cooling to -80 °C for 2 days. Upon removal of the supernatant via syringe and washing with 5 mL of cold hexane, 0.35 g pale yellow crystals of (Cp*Ru)₂(C₁₄H₂₀) were isolated corresponding to a yield of 53% based on [Cp*RuCl]₄.

¹H NMR (toluene-d_8, ambient): δ 4.93 (s, 2 H, H3), 2.47 (d of d, J = 12.9 Hz, 6.2 Hz, 2 H, -CH₂-), 2.23 (d, J = 2.4 Hz, 2 H, H1,5-exo), 2.15 (d, J = 2.4 Hz, 2 H, H1,5-exo), 1.98 (d of d, J = 12.9 Hz, 6.2 Hz, 2 H, -CH₂-), 1.75 (s, 6 H, -CH₃), 1.72 (s, 30 H, -CH₃(Cp*)), 0.39 (d, J = 2.4 Hz, 2 H, H1,5-endo), 0.35 (d, J = 2.4 Hz, 2 H, H1,5-endo).

¹³C NMR (toluene-d_8, ambient): δ 95.7 (s, C2,4), 91.8 (d, J = 152 Hz, C3), 91.5 (s, C2,4), 89.5 (s, C on Cp*), 46.5 (t, J = 123 Hz, -CH₂-), 45.0 (t, J = 153 Hz, C1,5), 44.2 (t, J = 151 Hz, C1,5), 25.7 (q, J = 127 Hz, -CH₃), 10.8 (q, J = 125 Hz, CH₃ on Cp*).

IR (Nujol mull): 3042 (w), 2985 (m, sh), 1943 (w), 1590 (w, br), 1472 (w), 1410 (m), 1258 (s), 1045 (s, br), 945 (w), 860 (m), 785 (s), 700 (s), 660 cm⁻¹ (sh).

MS (17 eV, EI) [m/z (relative intensity)]: 663 (77), 661 (82), 660 (98), 659 (95), 658 (100), 657 (86), 653 (82).

Anal. Calcd for C₃₄H₅₀Ru₂: C, 61.79; H, 7.62. Found: C, 61.42; H, 7.20.

Yb[4,4'-(CH₂)₂(2-C₆H₈)₂](THF)₂. A solution of 0.49 g (1.8 mmol) of K₂C₁₄H₂₀ in 40 mL of THF was added dropwise to a solution of 1.2 g (1.8 mmol) of YbI₂·3THF in 50 mL of THF at -78 °C. The reaction mixture was then stirred for an additional 15 h at room temperature. After removal of the KI, the dark red solution was concentrated to 50 mL and cooled slowly to -30 °C. During the next few days the product deposited as green cube-shaped crystals. A second fraction was obtained by concentrating and cooling down the supernatant. Yield: ~70%. A second product was observed to form as minute red crystals in very low yield. This second product could not be isolated in sufficient quantity for characterization but could possibly be either a product of the end-center-coupled dianion[9] or perhaps a mono(tetrahydrofuran) adduct of an alternative isomer in which the two dienyl ligands are present in a syn-eclipsed orientation (vide infra). The principal green product is very air-sensitive.

¹H NMR (THF-d_8, ambient): δ 3.91 (s, 2 H), 3.54 (br s, 4 H), 3.52 (s, 2 H), 3.45 (s, 2 H), 2.58 (m, 2 H, -CH₂-), 2.37 (m, 2 H, -CH₂-), 1.69 (s, 6 H).

¹³C NMR (THF-d_8, ambient): δ 148.8 (s), 143.8 (s), 90.0 (d, J = 153 Hz), 82.2 (t, J = 151 Hz), 77.8 (t, J = 153 Hz), 41.0 (t, J = 127 Hz), 28.1 (q, J = 123 Hz).

Anal. Calcd for C₂₂H₃₆O₂Yb: C, 52.27; H, 7.18. Calcd for C₁₈H₂₈OYb: C, 49.88; H, 6.51. Calcd for C₁₄H₂₀Yb: C, 46.53; H, 5.58. Found: C, 46.10; H, 6.16.

X-ray Diffraction Studies. The crystallographic studies were carried out on a Nicolet P1̄ diffractometer. Negligible decays in diffraction intensities were observed. The metal atom positions were determined from Patterson syntheses, after which the remaining non-hydrogen atoms were located from difference Fourier maps. Hydrogen atoms were placed either in idealized positions or in positions suggested by the difference Fourier maps, but their

locations were not refined. The thermal parameters for the hydrogen atoms were all set equal to 5 Å². Other pertinent data collection and structural refinement parameters are provided in Table I. Positional and metrical parameters are collected in Tables II–V.

Table I. Summary of the Diffraction Studies for [4,4'-(CH₂)₂(2-C₆H₈)₂][Ru(C₅Me₅)]₂ (II) and Yb[4,4'-(CH₂)₂(2-C₆H₈)₂](THF)₂ (III)

	II	III
formula	C₃₄H₅₀Ru₂	C₂₂H₃₆O₂Yb
mol wt	660.9	505.6
space group	*P2₁/c*	*C2/c*
lattice consts		
a, Å	13.727 (3)	13.852 (2)
b, Å	7.552 (2)	10.394 (1)
c, Å	15.135 (4)	16.807 (3)
β, deg	99.54 (1)	112.93 (1)
V, Å³	1547.3	2228.5
Z	2	4
d(calc), g/cm³	1.42	1.51
λ	0.710 73	0.710 73
temp, °C	20	20
cryst size, mm	0.23 × 0.20 × 0.15	0.30 × 0.27 × 0.10
linear abs coeff,/cm⁻¹	9.77	41.94
scan type	θ–2θ	θ–2θ
scan speed, deg/min	3.0	3.0
abs treatment	ψ scan	ψ scan
transm factors	0.606–1.358	0.507–1.000
2θ limits, deg	3–46	3–46
min hkl	0,0,-15	0,0,-19
max hkl	14,8,16	15,11,16
no. of unique obsd data	1382	1287
no. of variables	175	115
$R(F)$	0.076	0.043
$R_w(F)$	0.078	0.050
max diff Fourrier peak, e/Å³	1.32	0.80

Table II. Positional Parameters for the Non-Hydrogen Atoms of [4,4'-(CH₂)₂(2,2'-C₆H₈)][Ru(C₅Me₅)]₂

atom	x	y	z
Ru	-0.22395 (4)	0.07417 (9)	0.12638 (4)
C1	-0.1661 (6)	0.261 (2)	0.2292 (9)
C2	-0.1068 (7)	0.099 (2)	0.2439 (9)
C3	-0.0686 (7)	0.025 (2)	0.1705 (8)
C4	-0.0856 (7)	0.091 (1)	0.0799 (8)
C5	-0.1372 (6)	0.250 (1)	0.0571 (10)
C6	-0.0997 (12)	-0.006 (3)	0.3266 (10)
C7	-0.0506 (9)	-0.028 (2)	0.0081 (9)
C8	-0.3094 (8)	-0.147 (2)	0.0544 (7)
C9	-0.3210 (8)	-0.153 (1)	0.1458 (7)
C10	-0.3688 (6)	0.016 (2)	0.1648 (6)
C11	-0.3811 (6)	0.113 (1)	0.0849 (9)
C12	-0.3439 (7)	0.010 (2)	0.0179 (7)
C13	-0.2675 (13)	-0.303 (2)	0.0038 (10)
C14	-0.2993 (23)	-0.309 (2)	0.2113 (11)
C15	-0.4030 (8)	0.057 (3)	0.2490 (11)
C16	-0.4351 (8)	0.289 (2)	0.0697 (16)
C17	-0.3617 (8)	0.077 (2)	-0.0779 (9)

Results and Discussion

From a double deprotonation of 2,4,7,9-tetramethyl-1,3,7,9-decatetraene, readily prepared by the oxidative coupling of 2,4-C₇H₁₁ (C₇H₁₁ = dimethylpentadienyl) anions, one may isolate a pyrophoric, bridged bis(pentadienyl) dianion, I (Scheme I). As this dianion is far less soluble than typical pentadienyl monoanions in organic solvents such as THF, spectroscopic methods could not be utilized for its characterization. However, the dianion does react relatively cleanly with a variety of metal complexes, whose subsequent characterizations have served to confirm the formulation of I. Thus, the reaction with a half-equiv of [Ru(C₅Me₅)Cl]₄ leads to a bridged bimetallic compound (II), while from YbI₂ the chelating complex III is isolated (Scheme I).

Table III. Pertinent Bonding Parameters for
[4,4'-(CH$_2$)$_2$(2,2'-C$_6$H$_8$)$_2$][Ru(C$_5$Me$_5$)]$_2$

Bond Distances (Å)			
Ru–C1	2.153 (5)	C8–C9	1.419 (8)
Ru–C2	2.199 (5)	C8–C12	1.362 (8)
Ru–C3	2.158 (4)	C9–C10	1.486 (8)
Ru–C4	2.136 (4)	C10–C11	1.399 (8)
Ru–C5	2.165 (5)	C11–C12	1.436 (8)
C8–C13	1.566 (8)	C12–C17	1.515 (7)
C9–C14	1.534 (7)	C1–C2	1.468 (8)
Ru–C8	2.223 (5)	C2–C3	1.418 (9)
Ru–C9	2.222 (4)	C3–C4	1.442 (8)
Ru–C10	2.207 (4)	C4–C5	1.404 (7)
Ru–C11	2.164 (3)	C2–C6	1.472 (8)
Ru–C12	2.180 (4)	C4–C7	1.549 (8)
C10–C15	1.461 (9)	C7–C7'	1.514 (11)
C11–C16	1.524 (7)		

Bond Angles (deg)			
C1–C2–C3	118.5 (5)	C8–C12–C11	108.9 (4)
C1–C2–C6	122.5 (6)	C9–C8–C13	124.3 (6)
C3–C2–C6	118.2 (5)	C12–C8–C13	126.0 (5)
C2–C3–C4	125.9 (4)	C8–C9–C14	127.8 (6)
C3–C4–C5	121.6 (5)	C10–C9–C14	125.3 (6)
C3–C4–C7	116.4 (4)	C9–C10–C15	124.4 (5)
C5–C4–C7	121.8 (5)	C11–C10–C15	129.4 (5)
C4–C7–C7'	110.3 (6)	C10–C11–C16	124.9 (6)
C9–C8–C12	109.6 (4)	C12–C11–C16	125.9 (6)
C8–C9–C10	106.6 (4)	C8–C12–C17	132.0 (5)
C9–C10–C11	106.0 (4)	C11–C12–C17	118.4 (5)
C10–C11–C12	108.8 (4)		

Table IV. Positional Parameters for the Non-Hydrogen
Atoms of Yb[4,4'-(CH$_2$)$_2$(2-C$_6$H$_8$)$_2$](THF)$_2$

| atom	x	y	z
Yb	0.500	0.27759 (8)	0.250
O1	0.6084 (6)	0.4463 (8)	0.3394 (5)
C1	0.3846 (9)	0.3201 (14)	0.3599 (8)
C2	0.4539 (8)	0.2209 (14)	0.3942 (7)
C3	0.4620 (10)	0.1041 (13)	0.3551 (8)
C4	0.4025 (10)	0.0626 (12)	0.2718 (9)
C5	0.3139 (11)	0.1224 (15)	0.2014 (9)
C6	0.5403 (11)	0.2406 (16)	0.4841 (8)
C7	0.4398 (12)	-0.0621 (14)	0.2368 (11)
C8	0.7192 (10)	0.4511 (14)	0.3748 (9)
C9	0.7504 (11)	0.5498 (15)	0.4443 (19)
C10	0.6614 (13)	0.6333 (16)	0.4205 (10)
C11	0.5771 (15)	0.5594 (17)	0.3679 (15)

^{1}H and ^{13}C NMR spectra for **II** are consistent with the expected formulation as a bimetallic product. However, two sets of resonances are actually observed, which may be attributed to the presence of two isomers, **IIa** and **IIb**,

IIa (*C$_i$*)   **IIb (*C$_2$*)**
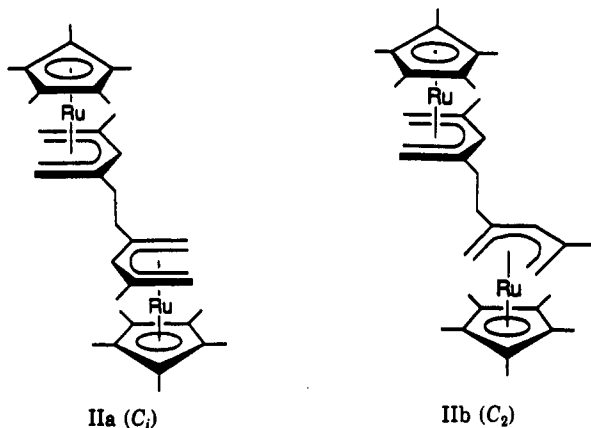
one significantly more abundant than the other (ca. 6:1 for the isolated product). The major resonances found in the ^{13}C NMR spectra consist of three quaternary, one CH, three CH$_2$, and two CH$_3$ environments. The ^{13}C–H coupling constants reveal formal sp^2 hybridization for the CH

Table V. Pertinent Bonding Parameters for
Yb[4,4'-(CH$_2$)$_2$(2-C$_6$H$_8$)$_2$](THF)$_2$

Bond Distances (Å)			
Yb–C1	2.909 (9)	C2–C3	1.406 (14)
Yb–C2	2.799 (8)	C2–C6	1.533 (13)
Yb–C3	2.715 (10)	C3–C4	1.387 (15)
Yb–C4	2.709 (9)	C4–C5	1.469 (16)
Yb–C5	2.876 (10)	C4–C7	1.592 (15)
Yb–O	2.414 (6)	C7–C7'	1.550 (26)
O–C8	1.415 (11)	C8–C9	1.487 (13)
O–C11	1.400 (13)	C9–C10	1.431 (16)
C1–C2	1.373 (12)	C10–C11	1.390 (16)

| Bond Angles (deg)			
O–Yb–O	86.8 (3)	C5–C4–C7	109.6 (12)
C1–C2–C3	128.5 (10)	C4–C7–C7'	111.2 (10)
C1–C2–C6	117.6 (10)	C8–O–C11	104.9 (8)
C3–C2–C6	113.7 (9)	O–C8–C9	106.8 (8)
C2–C3–C4	128.0 (10)	C8–C9–C10	104.1 (9)
C3–C4–C5	131.5 (11)	C9–C10–C11	105.1 (10)
C3–C4–C7	118.4 (13)	O–C11–C10	112.8 (11)
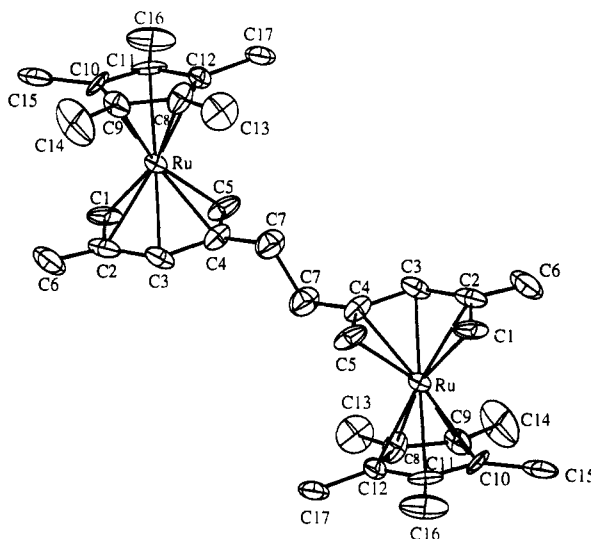
Figure 1. Perspective view and numbering scheme for [4,4'-(CH$_2$)$_2$(2-C$_6$H$_8$)$_2$][Ru(C$_5$Me$_5$)]$_2$. The molecule possesses crystallographic *C$_i$* symmetry.

Scheme I
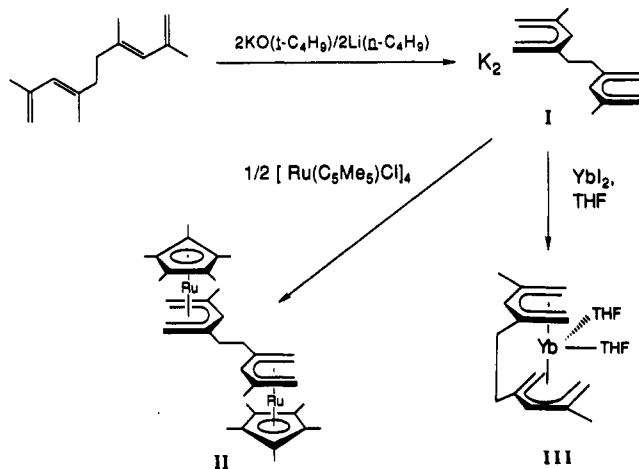
and two of the CH$_2$ groups and formal sp^3 hybridization for the third CH$_2$ and the CH$_3$ groups, demonstrating that the deprotonation has indeed produced the bridged bis-(pentadienyl) dianion (**I**), rather than some other alternative, such as a fully conjugated decapentaene dianion, which could arise from deprotonation of the central CH$_2$ groups.

An X-ray diffraction study has been carried out on II (Figure 1) and does indeed reveal a bimetallic compound in which two Ru(C$_5$Me$_5$) fragments are linked by the bridged bis(pentadienyl) group. The two halves of the molecule are related by a crystallographic center of inversion, demonstrating that the major isolated isomer is IIa.[10] The "half-open metallocene" centers are twisted ca. 3.2° from an ideally staggered configuration, whereas Ru(C$_5$H$_5$)(2,4-C$_7$H$_{11}$) appeared to be eclipsed, or nearly so.[11] The M–C distances for the open ligand average 2.162 (2) Å, significantly less than that of 2.199 (2) Å for the C$_5$Me$_5$ ligand. Somewhat similar values, 2.168 (3) vs 2.178 (3) Å, were observed for Ru(C$_5$H$_5$)(2,4-C$_7$H$_{11}$). For the most part, the Ru–C distances are fairly regular, the exceptions being the short Ru–C11 bond and the differences in the Ru–C2 and Ru–C4 bond lengths. The short Ru–C(11) bond is likely the result of C11's location near the less congested, open dienyl edge, while the difference in Ru–C2 and Ru–C4 bond lengths may arise from the bridging group attached to C4.

The bonding parameters for the ligands are not unusual.[12] The interior C–C–C angle about C3 is larger than those about C2 and C4. Both C6 and C7 are bent out of the dienyl ligand plane by ca. 0.23 Å toward the metal atom, corresponding to an average tilt of 9.0°. The C$_5$Me$_5$ methyl groups are tilted away from the metal atom, by an average of 5.5° for C15–17 but only 3.3° for C13,14.

For the ytterbium(II) complex, spectral and analytical data did not unambiguously define the stoichiometry relative to the number of coordinated THF molecules, quite possibly due to the loss of THF from the crystalline solid. Two formulations seemed possible, III and IV, de-

III (*C$_2$*)   IV (*C$_s$*)
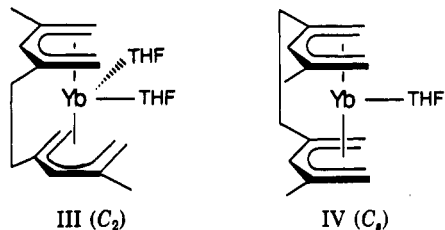
pending on the relative orientations of the dienyl ligands. In either case, the two dienyl fragments would be related by symmetry to one another, in accord with the observation of eight ^{1}H and seven ^{13}C NMR signals for the dienyl ligands.

While the NMR spectra do not allow us to distinguish between the two possible structures, there are some interesting observations to be made about the positions of the various resonances. For typical diamagnetic open metallocenes, e.g., M(2,4-C$_7$H$_{11}$)$_2$ (M = Fe, Ru, Os, Ti),[13] the H1,5-endo resonances are found most upfield, in the range between ±2 δ.
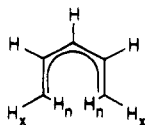

Figure 2. Perspective view and numbering scheme for Yb-[4,4'-(CH$_2$)$_2$(2-C$_6$H$_8$)$_2$](THF)$_2$. The molecule resides on a C_2 axis of symmetry.

For III, however, all of the H1,5-endo resonances are found with the H1,5-exo resonances in the range 3.45–3.54 ppm, while the H3 resonance was revealed by decoupling experiments to lie at 3.91 ppm. Such locations are more typical of salts such as K(2,4-C$_7$H$_{11}$)[14] and seem to reflect a high degree of ionic character in the pentadienyl fragments. Some interesting differences are also found in the ^{13}C NMR spectra. Although the locations of the dienyl CH and CH$_2$ resonances are reasonably similar to those of the transition-metal open metallocenes, the quaternary C2,4 resonances (143.8, 148.8 ppm) are significantly downfield those of the M(2,4-C$_7$H$_{11}$)$_2$ compounds (Fe, 99.2 ppm; Ti, 122.3 and 125.1 ppm). This may well arise from the lack of a back-bonding capability in complexes involving lanthanide metal ions. Not surprisingly, perhaps, all of the ^{13}C resonances for the ytterbium compound are found near to the observed positions for K(2,4-C$_7$H$_{11}$) (C1,5, 77.4 ppm; C2,4, 144.5 ppm; C3, 83.4 ppm).

The structure of III is shown in Figure 2. The Yb center is coordinated by two η^5-dienyl fragments and two THF molecules, each pair related by a crystallographically imposed C_2 axis. Notably, bis(ligand) adducts of open metallocenes are relatively rare, two examples being Zr-(C$_5$H$_7$)$_2$(dmpe) and Zr(2,4-C$_7$H$_{11}$)$_2$(CO)$_2$.[15] While mono-(ligand) adducts have nearly parallel dienyl ligand planes, this is not found for the bis(ligand) counterparts.[16] In this case an angle of 50.6 (4)° is observed, quite similar to the value of 50.2 (8)° in [1,3-(CH$_2$)$_3$(C$_5$H$_4$)$_2$]Yb(THF)$_2$ (V).[17] A twist of 84.8 (4)° occurs between the two dienyl ligands, 35.2° away from the ideal 120° value for III.[18] This may be compared to the 58.1 (12)° torsion angle about the C7–C7' bond and the O–Yb–O' angle of 86.8 (3)°. The similarity of the twist and O–Yb–O' angles allows the two THF molecules to each reside by the open edge of a dienyl ligand. For comparison, the O–Yb–O' angle in V is 82.4 (5)°.

The Yb–O distance of 2.414 (6) Å is essentially identical with that of 2.415 (10) Å in V. However, the average Yb–C bond distance of 2.80 Å is clearly larger than that of 2.697 (7) Å in V, suggesting weaker bonding for the open ligand, in contrast to the situation generally observed for transition

(10) Recrystallization of the 6:1 mixture led to preferential crystallization of the major isomer, while the minor isomer remained in solution. NMR spectroscopy demonstrated that the isolated solid contained only the major isomer. Hence, the X-ray study could not have been carried out on a crystal of the minor isomer.

(11) Gleiter, R.; Hyla-Kryspin, I.; Ziegler, M. L.; Sergeson, G.; Green, J. C.; Stahl, L.; Ernst, R. D. *Organometallics* **1989**, *8*, 298.

(12) Ernst, R. D. *Struct. Bonding (Berlin)* **1984**, *57*, 1.

(13) (a) Wilson, D. R.; Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1983**, *2*, 1220. (b) Stahl, L.; Ernst, R. D. *Ibid.* **1983**, *2*, 1229. (c) Stahl, L.; Ma, H.; Ernst, R. D.; Hyla-Kryspin, I.; Gleiter, R.; Ziegler, M. L. *J. Organomet. Chem.* **1987**, *326*, 257.

(14) Yasuda, H.; Yamauchi, M.; Ohnuma, Y.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1481.

(15) Waldman, T. E.; Stahl, L.; Arif, A. M.; Rheingold, A. L.; Ernst, R. D. Unpublished results.

(16) (a) Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1255. (b) The steric demands of the open dienyl ligands are increased further in the lanthanide complexes by their relatively large C–C–C angles.

(17) Swamy, S. J.; Loebel, J.; Schumann, H. *J. Organomet. Chem.* **1989**, *379*, 51.

(18) The twist (or conformation) angle is the angle formed between the two Yb–C3–($^1/_2$C1 + $^1/_2$C5) planes.

metals.[16] Such apparently weaker metal–pentadienyl bonding is not surprising in these somewhat crowded compounds, due to the greater size of the pentadienyl ligand and the closer proximity of these ligands to the metal center (2.330 vs 2.415 (10) Å). A similar claim has been made for weaker uranium bonding to the open dienyl ligands in $U(2,4\text{-}C_7H_{11})_3$ relative to $U(C_5H_5)_3(THF)$.[19] However, this conclusion was reached through competitive ligand/anion exchange reactions, and the observed favorability of the latter complex may derive instead from the presence of the additional U–O bond, which could be tolerated in the less crowded cyclopentadienyl compound. Nonetheless, the observation of significantly shorter U–C distances in $U(C_5H_5)(BH_4)_3$ relative to $U(2,4\text{-}C_7H_{11})(BH_4)_3$ suggests that the uranium–pentadienyl bonding is probably weaker than the $U\text{-}C_5H_5$ bonding.[18] Such a situation does not seem unusual given the coordinate saturation that is generally found for organoactinide compounds and the much greater steric demands imposed by pentadienyl groups relative to C_5H_5 and even C_5Me_5 ligands.[16]

The relative values of the C3, C2,4, and C1,5 bond distances are quite unusual, as the C3 distance is the shortest (on average) and the bond lengths become progressively longer as one moves out to the termini of the pentadienyl ligands. Such a pattern has not been seen previously and apparently reflects the unusual character of the Ln(II)–pentadienyl bonding and perhaps as well a great deal of steric crowding. Notably, a similar pattern exists for the η^5-dienyl ligand in $Yb[\eta^5\text{-}1,5\text{-}(Me_3Si)_2C_5H_5][\eta^3\text{-}(Me_3Si)_2C_5H_5](diglyme)$,[20] for which the Yb–C1–5 bond lengths fall in the order 2.919 (10), 2.703 (11), 2.594 (11), 2.728 (11), and 3.045 (10) Å. Interestingly, for the Nd(III) complex $Nd(2,4\text{-}C_7H_{11})_3$, the Nd–C bond lengths fall in the order Nd–C3 < Nd–C1,5 < Nd–C2,4, reflecting the relative charges of the carbon atoms.[21] It may be that in these relatively ionic metal compounds the central carbon atom of the dienyl ligand, being most negatively charged, binds most strongly to the metal, with much less interaction occurring for the formally uncharged C2,4 atoms, leading to the dienyl plane becoming progressively removed from the metal ion, as observed for Yb(II).[22] However, the stronger Lewis acid Nd(III) apparently exerts enough of an attraction for the C1,5 atoms that they are pulled back toward the metal center.

The above results demonstrate that bis(pentadienyl) groups may indeed function both as bridging units for bimetallic compounds and as chelating ligands for single metal centers. It can be expected that these ligands will find a number of applications in organometallic chemistry, much as their cyclopentadienyl analogues have. Indeed, we have succeeded in preparing a number of related complexes involving both early and late transition metals[23] and have found in some cases that their chemistry differs significantly from that of their unbridged analogues.

Supplementary Material Available: Tables of thermal and hydrogen atom parameters and least-squares-plane data (8 pages); tables of structure factors (10 pages). Ordering information is given on any current masthead page.

(19) Baudry, D.; Bulot, E.; Charpin, P.; Ephritikhine, M.; Lance, M.; Nierlich, M.; Vigner, J. *J. Organomet. Chem.* **1989**, *371*, 163.

(20) Kunze, K.; Arif, A. M.; Ernst, R. D. Unpublished results.

(21) (a) Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1982**, *1*, 708. (b) Additional comparisons may be made with related lanthanide(III) allyl and pentadienyl compounds.[21c,d] (c) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2314. (d) Schumann, H.; Dietrich, A. *J. Organomet. Chem.* **1991**, *401*, C33.

(22) (a) A reviewer has questioned the appropriateness of designating the ytterbium–dienyl interaction as η^5 in view of the long Yb–C1,5 bonds. It can be noted that the Yb–C1,5 bonds for the η^5-U ligand in $Yb[\eta^5\text{-}1,5\text{-}(Me_3Si)_2C_5H_5][\eta^3\text{-}1,5\text{-}(Me_3Si)_2C_5H_5](diglyme)$ are even longer but must be considered appreciable, since they seem to hold the ligand in the U conformation, which is not favored for the free anion, and also lead to two bulky Me_3Si groups remaining near the coordination sphere.[22b] Thus, were the Yb–C1,5 interactions negligible, conversion to an η^3-bonding mode should be favored, which would leave two formally charged carbon atoms near the metal center. (b) An indication of a tendency to keep the Me_3Si substituents away from the coordination sphere can be seen in some transition-metal chemistry. Thus, while $Ta(C_5H_5)_2(\eta^3\text{-Pdl})$ has both terminal carbon atoms bound to the metal for Pdl = $2,3\text{-}C_7H_{11}$, the complex for which Pdl = $1,5\text{-}(Me_3Si)_2C_5H_5$ possesses the more normal η^3-allyl coordination. Hence, it appears unreasonable for a complex to retain the Me_3Si substituents near the coordination sphere unless significant compensation was achieved.

(23) Weng, W.-Q.; Arif, A. M.; Ernst, R. D. Unpublished results.