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Bridged Bis(pentadienyl) Ligands: Conformationally Altered Open Metallocenes

Wei-qing Weng, Atta M. Arif, and Richard D. Ernst*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

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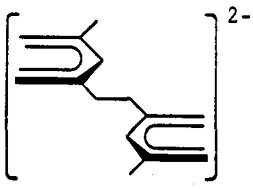
The reactions of the bridged bis(pentadienyl) dianion, $K_2[4,4'-(CH_2)_2(2-C_6H_8)_2]$ ($2-C_6H_8$ = 2-methylpentadienyl) with chlorides of divalent vanadium, chromium, or iron lead to the expected bridged open metallocene complexes, $M[4,4'-(CH_2)_2(2-C_6H_8)_2]$, whose stabilities and reactivities differ significantly from those of the $M(2,4-C_7H_{11})_2$ counterparts. Thus, the chromium complex readily forms a variety of ligand adducts, whereas $Cr(2,4-C_7H_{11})_2$ forms none. Structural data have been obtained for the vanadium and chromium compounds. For $V[4,4'-(CH_2)_2(2-C_6H_8)_2]$, the space group is orthorhombic, *Pbcn*, with a = 10.941(3) Å, b = 13.579(2) Å, c = 8.424(2) Å, and V = 1251.53 Å^3 for z = 4. Discrepancy indices of R = 0.027 and R_w = 0.028 were obtained for 804 observed reflections. For $Cr[4,4'-(CH_2)_2(2-C_6H_8)_2]$, the space group at −130° is orthorhombic, *Pbca*, with a = 8.499(2) Å, b = 17.091(2) Å, c = 33.569(6) Å, and V = 4875.92 Å^3 for Z = 16 (two independent molecules). Discrepancy indices of R = 0.054 and R_w = 0.058 were obtained for 2790 observed reflections. The structural results reveal that a great deal of strain in the organic fragment is required to bring about effective bonding with the metal centers.

Bridged bis(cyclopentadienyl) ligands have found extensive applications in the field of organometallic chemistry. Very significant changes in structure and chemistry are quite often observed, whether these ligands are bound to transition metals,[1] lanthanides,[2] or actinides.[3] A particularly notable example is the use of these complexes for the stereospecific polymerization of α-olefins.[4] More recently, it has been demonstrated that a bridged bis(pentadienyl) dianion, I, may also be prepared and used as a source of the appropriate ligand for various metal or dimetal complexes.[5] In the former situation, the bridged bis(pentadienyl) ligand chelates a single metal center, e.g., $Yb^{II}(THF)_2$, while in the latter case, it serves to bridge two metal centers, e.g., $Ru(C_5Me_5)$. We now report that this ligand may be used to chelate various transition metal centers, leading to what may be regarded as "conformationally altered" open metallocenes. The properties and chemistry of these species have been found to be quite different from those of their nonbridged open metallocene analogs, $M(2,4-C_7H_{11})_2$ (C_7H_{11} = dimethylpentadienyl).[6]



I

Experimental Section

All operations involving organometallics were carried out under an atmosphere of prepurified nitrogen or in a glovebox. Solvents were thoroughly dried and deoxygenated by standard procedures. Spectroscopic studies were carried out as previously described.[7] Numbers of carbon atoms associated with given ^{13}C NMR resonances are reported in accord with their assignments but were not precisely integrated. Analytical data were obtained by Beller Labs. $FeCl_2$,[8] $CrCl_3(THF)_3$,[9] $VCl_3(THF)_3$,[10] and $K_2[4,4'-(CH_2)_2(2-C_6H_8)_2]$[5] were prepared by reported procedures.

$V[4,4'-(CH_2)_2(2-C_6H_8)_2]$. A 100-mL, three-neck flask was charged with 0.75 g (2.0 mmol) of $VCl_3(THF)_3$ and 40 mL of THF. The resulting dark red solution was stirred at room temperature for 4 h with excess Zn powder, producing a green slurry of the divalent vanadium complex, $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$.[11] The green slurry was then cooled to −78°C, and a slurry of 0.54 g (2.0 mmol) of $K_2[4,4'-(CH_2)_2(2-C_6H_8)_2]$ in 20 mL of THF was added dropwise via a pressure-equalizing dropping funnel with stirring. The mixture was kept stirring at −78 °C for 0.5 h and then warmed to room temperature, at which time it was allowed to stir for an additional 4 h, producing a dark green solution. After the solvent was removed in vacuo, the product was extracted with three 30-mL portions of pentane. The combined extracts were filtered through a pad of Celite on a frit to give a dark green solution. After the solvent was removed in

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vacuo, the dark green crystalline product was sublimed at 50–55 °C under vacuum, yielding 0.10 g (0.41 mmol, mp 62–64 °C), corresponding to a 21% yield based on $VCl_3(THF)_3$.

IR (Nujol mull): 3050 (w), 1310 (m), 1255 (w), 1180 (m, sh), 1145 (m), 1030 (w, sh), 1025 (m), 987 (m), 970 (m), 905 (m), 880 (s), 855 (s), 839 (m), 826 (s), 818 (m, sh), 795 (w), 780 (w, sh), 765 (m), 753 (w), 712 (s), 700 (w) cm^{-1}. Mass spectrum (EI, 17 eV), *m/z* (relative intensity): 239 (100), 236 (10), 235 (75), 143 (15). ESR data (toluene ambient): $g = 1.982, A_v = 69.4$ G. Anal. Calcd for $C_{14}H_{20}V$: C, 70.28; H, 8.43. Found: C, 70.32; H, 8.51.

$Cr[4,4'-(CH_2)_2(2-C_6H_8)_2]$. This compound was synthesized in a manner analogous to that used for $V[4,4'-(CH_2)_2(2-C_6H_8)_2]$. To a solution of 0.75 g (2.0 mmol) of $CrCl_3(THF)_3$ in 30 mL of THF was added 0.1 g (excess) of zinc powder. The mixture was stirred until all the purple $CrCl_3$ had been reduced to light blue "$CrCl_2$". The slurry of "$CrCl_2$" was cooled to −78 °C, and a slurry of 0.54 g (2.0 mmol) of $K_2[4,4'-(CH_2)_2(2-C_6H_8)_2]$ in 20 mL of THF was added. The resulting bright green solution was stirred for 0.5 h at −78 °C, warmed to room temperature, and then stirred for an additional 2 h. Upon completion of the reaction, a workup analogous to that for the compound above yielded 0.12 g (0.50 mmol) of the title compound as dark green crystals (25% based on $CrCl_3(THF)_3$, mp 45–47 °C).

IR (Nujol mull): 3084 (w), 3066 (m), 3020 (w, sh), 2720 (w), 1505 (m), 1273 (w), 1192 (w), 1028 (s), 1001 (s), 979 (w), 866 (m, sh), 858 (s), 828 (m), 812 (m), 720 (w), 620 (m, sh) cm^{-1}. Mass spectrum (EI, 17 eV), *m/z* (relative intensity): 240 (50), 238 (12), 237 (13), 236 (100), 144 (12), 52 (42). Anal. Calcd for $C_{14}H_{20}Cr$: C, 69.97; H, 8.38. Found: C, 69.73; H, 8.26.

An orange byproduct is sometimes formed in very small quantities from this reaction and deposits first as very small crystals from the hydrocarbon solutions. A structural determination (Cu Kα radiation, rotating anode) revealed a $M_3[\eta^5,\eta^{5'}-4,4'-(CH_2)_2(2-C_6H_8)_2]_2$ structure very similar to that observed for $Mn_3(3-C_6H_9)_4$.[12] It is therefore possible that the low-yield product arises from a small manganese content in the chromium chloride starting materials. Structural details[13] for this compound are provided in the supplementary material.

$Cr[\eta^5,\eta^{3'}-4,4'-(CH_2)_2(2-C_6H_8)_2](CO)_2$. A 100-mL, two-neck round-bottom flask equipped with a gas inlet and magnetic stirring bar was charged with 0.060 g (0.20 mmol) of $Cr[4,4'-(CH_2)_2(2-C_6H_8)_2]$ and placed under a carbon monoxide atmosphere. Subsequently, 50 mL of pentane was added to the flask with stirring. The solution changed color from bright green to yellow orange in ca. 10 min, and carbon monoxide was steadily absorbed, as evidenced by an attached bubbler. The resulting yellow orange solution was allowed to stir under the carbon monoxide atmosphere for an additional 0.5 h. Following the filtration of the product solution through a pad of Celite on a frit, the solvent was removed in vacuo. The dicarbonyl complex, $Cr[4,4'-(CH_2)_2(2-C_6H_8)_2](CO)_2$, may be sublimed and isolated in fair yield as a yellow orange oil at 50–55 °C under vacuum.

^1H NMR (benzene-d_6, ambient): δ 5.07 (s, 1 H), 4.68 (s, 2 H), 4.38 (s, 1 H), 3.24 (s, 1 H), 2.84 (s, 1 H), 2.47 (s, 1 H), 2.38 (s, 1 H), 1.96 (s, 3 H), 1.79 (s, 3 H), 1.70 (m, 2 H, $-CH_2-$), 1.45 (m, 2 H, $-CH_2-$), −0.11 (s, 1 H), −0.31 (s, 1 H).

^{13}C NMR (benzene-d_6, ambient): δ 246.1 (s, CO), 244.5 (s, CO), 144.8 (s, C(2 or 4)), 127.4 (s, C(2 or 4)), 118.1 (s, C(2 or 4)), 108.8 (t, J = 158 Hz, C(1 or 5)), 104.6 (s, C(2 or 4)), 102.8 (d, J = 156 Hz, C(3)), 86.5 (d, J = 153 Hz, C(3)), 67.6 (t, J = 157 Hz, C(1 or 5)), 61.4 (t, J = 157 Hz, C(1 or 5)), 46.2 (t, J = 156 Hz, C(1 or 5)), 39.3 (t, J = 123 Hz, $-CH_2-$), 34.0 (t, J = 128 Hz, $-CH_2-$), 27.0, (q, J = 131 Hz, CH_3), 23.2 (q, J = 135 Hz, CH_3). IR (neat): 3082 (m), 2960 (s), 2918 (s), 2868 (m), 1961 (s), 1890 (s), 1612 (m), 1595 (m, sh), 1490 (m), 1442 (s), 1376 (s), 1323 (m), 1304 (w), 1255 (m), 1210 (w), 1141 (w), 1030 (m), 1005 (w, sh), 954 (w), 925 (w), 889 (s), 869 (m, sh), 798 (w), 695 (w), 660 (m), 647 (s), 615 (m) cm^{-1}. Mass spectrum (EI, 17 eV), *m/z* (relative intensity): 296 (4), 268 (3), 240 (43), 237.5 (14), 236 (100), 52 (52).

$Fe[4,4'-(CH_2)_2(2-C_6H_8)_2]$. The title compound may be synthesized by the general method for preparing the homoleptic bridged bis(pentadienyl)metal complexes of vanadium and chromium, which involves the reaction of the potassium salt of the bis(pentadienyl) dianion, $K_2[4,4'-(CH_2)_2(2-C_6H_8)_2]$, with 1 equiv of anhydrous ferrous chloride, $FeCl_2$.

In preparation of the bis(pentadienyl)iron complex, $K_2[4,4'-(CH_2)_2(2-C_6H_8)_2]$ was added to a pale gray slurry of 2 equiv of $FeCl_2$ in THF at −78 °C via a solid addition funnel. The resulting dark red reaction mixture was warmed to room temperature and stirred for an additional 2 h. The solvent was removed in vacuo, and the product was extracted with two 30-mL portions of pentane. After removal of the solvent from the extracts, the iron complex could be sublimed as an oily red liquid at 60 °C under vacuum (17% crude yield).

NMR spectroscopic studies revealed that this compound exists in two isomeric forms. The major isomer could be isolated pure from the mixture by slow sublimation at 45–50 °C under vacuum.

^1H NMR (benzene-d_6, ambient): isomer 1 (major) δ 5.43 (s, 2 H, H(3)), 3.72 (s, 2 H, H(1 or 5-exo)), 2.58 (s, 2 H, H(1 or 5-exo)), 2.51 (s, 6 H, CH_3), 2.16 (m, 4 H, $-CH_2-$), −0.17 (s, 2 H H(1 or 5-endo)), −0.49 (s, 2 H, H(1 or 5-endo)); isomer 2 (minor) δ 5.16 (s, 2 H, H(3)), 3.32 (s, 2 H, H(1 or 5-exo)), 2.21 (s, 2 H, H(1 or 5-exo)), 1.70 (m, 4 H, $-CH_2-$), 1.52 (s, 2 H, H(1 or 5-endo)), 1.37 (s, 6 H, CH_3), −0.10 (s, 2 H, H(1 or 5-endo)). ^{13}C NMR (benzene-d_6, ambient): isomer 1 (major) δ 106.0 (s, C(2 or 4)), 100.1 (d, J = 161 Hz, C(3)), 98.5 (s, C(2 or 4)), 62.2 (t, J = 162 Hz, C(1 or 5)), 53.7 (t, J = 153 Hz, C(1 or 5)), 38.4 (t, J = 132 Hz, $-CH_2-$), 28.6 (q, J = 128 Hz, CH_3); isomer 2 (minor) δ 103.4 (s, C(2 or 4)), 95.9 (s, C(2 or 4)), 94.9 (d, J = 153 Hz, C(3)), 53.7 (t, J = 153 Hz, C(1 or 5)), 43.4 (t, J = 161 Hz, C(1 or 5)), 38.5 (t, J = 132 Hz, $-CH_2-$), 25.0 (q, J = 125 Hz, CH_3). IR (neat): 3100 (m), 3052 (m), 3020 (m, sh), 2920 (s, br), 2865 (s), 2721 (w), 1790 (br, w), 1642 (m), 1494 (s), 1440 (s), 1371 (s), 1352 (m), 1318 (m), 1257 (m), 1192 (w), 1138 (w), 1039 (m, sh), 1025 (m), 1000 (m), 979 (m), 933 (m), 920 (m), 888 (s), 826 (m), 803 (w), 784 (w), 732 (w), 698 (w), 646 (w), 628 (w) cm^{-1}. Mass spectrum (EI, 17 eV), *m/z* (relative intensity): 244 (100), 242 (20), 240 (19), 202 (14), 162 (85), 148 (58), 145 (11), 105 (12), 96 (15), 93 (13), 91 (45), 79 (14), 77 (13), 56 (22). High-resolution MS: calcd, 244.0914 amu; found, 244.0910 amu.

X-ray Diffraction Studies. Single crystals of the compounds were grown by slow vacuum sublimation at 30–35 °C. For the chromium compound, a crystal was attached to a glass fiber and transferred to an Enraf-Nonius CAD4 rotating anode diffractometer, where unit cell determination and data collection were carried out (at −130 °C). No significant change in standard reflection intensities was noticed during data collection. The chromium atom positions (two independent but essentially equal molecules) were readily determined by the Patterson method, after which the other atoms were located from difference Fourier maps. The hydrogen atoms were located and included in structure factor calculations, but their positions were not refined. For the vanadium compound, a single crystal was mounted under nitrogen in a glass capillary and transferred to a Nicolet-Siemens $P\bar{1}$ diffractometer for unit cell determination and data collection. No significant change in standard reflection intensities occurred. The vanadium atom position was determined by the Patterson method, after which the remaining atoms were located from difference Fourier maps. All hydrogen atoms were subjected to positional refinement with fixed thermal parameters. The molecule was found to possess crystallographically imposed C_2 symmetry. Other pertinent data collection and structure refinement parameters are provided in Table I. Positional and metrical parameters are presented in Tables II–V.

Results

The reactions of $K_2[4,4'-(CH_2)_2(2-C_6H_8)_2]$ with 2 equiv of various divalent metal halide complexes lead to the

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(13) The space group is $P2_1/n$ with a = 8.550(1) Å, b = 18.714(2) Å, c = 15.333(1) Å, β = 92.54(1)°, and V = 2451.0 Å^3 for Z = 4.

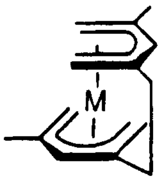
Table I. Summary of the Diffraction Studies for M[4,4′-$(CH_2)_2(2\text{-}C_6H_8)_2$] Complexes (M = Cr, A; M = V, B)

	A	B
formula	$C_{14}H_{20}Cr$	$C_{14}H_{20}V$
mol wt	240.3	239.3
space group	*Pbca*	*Pbcn*
lattice constants		
a, Å	8.499(2)	10.941(3)
b, Å	17.091(2)	13.579(2)
c, Å	33.569(6)	8.424(2)
V, Å^3	4875.9	1251.5
Z	16	4
d(calc), g/cm^3	1.31	1.27
λ	1.540 56	0.710 73
temp, °C	−130	16
cryst size, mm	0.20 × 0.18 × 0.08	0.75 × 0.28 × 0.18
linear abs coeff, cm^{-1}	75.4	7.3
scan type	θ–2θ	θ–2θ
scan speed, deg/min	3	3
abs treatment	ψ scan	ψ scan
rel transm factors	0.863–1.216	0.915–0.998
2θ limits, deg	4–130	2–50
min *hkl*	000	000
max *hkl*	7,20,39	12,16,10
unique, obsd data	2790	804
variables	272	99
R(*F*)	0.054	0.027
R_w(*F*)	0.058	0.029
max diff Fourier peak, e/Å^3	0.52	0.51

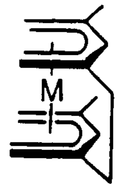
Table II. Positional Parameters for the Non-Hydrogen Atoms of V[4,4′-$(CH_2)_2(2\text{-}C_6H_8)_2$]

atom	*x*	*y*	*z*	*B* (Å^2)
V	0.000	0.13228(4)	0.250	2.95(1)
C(1)	0.1364(2)	0.0350(2)	0.1394(4)	4.32(6)
C(2)	0.1997(2)	0.1200(2)	0.1883(3)	3.72(5)
C(3)	0.1623(2)	0.2189(2)	0.1676(3)	3.96(5)
C(4)	0.0518(2)	0.2562(2)	0.1014(3)	3.66(5)
C(5)	−0.0271(2)	0.1976(2)	0.0116(3)	4.04(6)
C(6)	0.3073(2)	0.1040(2)	0.2974(4)	5.19(7)
C(7)	0.0082(3)	0.3569(2)	0.1587(3)	4.79(6)

formation of the respective ligand-bridged open metallocenes, M[4,4′-$(CH_2)_2(2\text{-}C_6H_8)_2$] (M = V, Cr, Fe), each of which could potentially exist in two isomeric forms, II and III. The products are readily sublimable, and possess



IIa (M = V)
b (M = Cr)
c (M = Fe)



IIIa (M = V)
b (M = Cr)
c (M = Fe)

colors which are similar to those of the analogous unbridged open metallocenes M(2,4-C_7H_{11})$_2$, although the bridged vanadium and chromium complexes seem to be "cleaner" shades of emerald green than their counterparts and look more like Ti(2,4-C_7H_{11})$_2$. Interestingly, the melting points increase from the iron compound to chromium and vanadium (an oil, 45–47 and 62–64 °C), whereas the reverse is observed for the M(2,4-C_7H_{11})$_2$ compounds, the titanium compound being an oil and the melting points rising steadily from there to the iron compound. Also interesting is the fact that the bridged chromium compound appears stable in air for hours, unlike Cr(2,4-C_7H_{11})$_2$, whereas the iron compounds follow the reverse trend.

Table III. Pertinent Bond Distances (Å) and Angles (deg) for V[4,4′-$(CH_2)_2(2\text{-}C_6H_8)_2$]

Distances			
V–C(1)	2.199(2)	C(2)–C(3)	1.415(2)
V–C(2)	2.252(1)	C(2)–C(6)	1.510(2)
V–C(3)	2.240(2)	C(3)–C(4)	1.424(2)
V–C(4)	2.172(2)	C(4)–C(5)	1.396(2)
V–C(5)	2.215(2)	C(4)–C(7)	1.526(2)
C(1)–C(2)	1.407(2)	C(7)–C(7)	1.548(2)
Angles			
C(1)–C(2)–C(3)	126.9(1)	C(3)–C(4)–C(5)	122.3(1)
C(1)–C(2)–C(6)	116.4(2)	C(3)–C(4)–C(7)	117.4(2)
C(3)–C(2)–C(6)	115.9(2)	C(5)–C(4)–C(7)	119.3(2)
C(2)–C(3)–C(4)	129.1(1)	C(4)–C(7)–C(7)	110.5(1)

Table IV. Positional Parameters for the Non-Hydrogen Atoms of Cr[4,4′-$(CH_2)_2(2\text{-}C_6H_8)_2$]

atom	*x*	*y*	*z*	*B* (Å^2)
Cr	0.2494(2)	0.21943(5)	0.09152(2)	2.58(2)
C(1)	0.3597(8)	0.3339(3)	0.0858(2)	3.0(1)
C(2)	0.3094(8)	0.3083(3)	0.0474(2)	2.9(1)
C(3)	0.3384(8)	0.2330(4)	0.0312(2)	3.0(1)
C(4)	0.4092(8)	0.1672(4)	0.0507(2)	3.2(1)
C(5)	0.4947(9)	0.1753(4)	0.0852(2)	3.2(1)
C(6)	0.1285(9)	0.2327(3)	0.1486(2)	3.3(1)
C(7)	0.1884(8)	0.1545(3)	0.1454(2)	2.8(1)
C(8)	0.1719(8)	0.1052(3)	0.1113(2)	2.7(1)
C(9)	0.1061(8)	0.1244(3)	0.0740(2)	2.8(1)
C(10)	0.0113(8)	0.1910(4)	0.0685(2)	3.1(1)
C(11)	0.1971(9)	0.3598(4)	0.0242(2)	3.7(2)
C(12)	0.3516(9)	0.0859(4)	0.0365(2)	3.5(1)
C(13)	0.1734(8)	0.0805(4)	0.0377(2)	3.3(1)
C(14)	0.2966(8)	0.1257(4)	0.1775(2)	3.5(2)
Cr′	0.7472(2)	0.39150(5)	0.15916(2)	2.61(2)
C(1)′	0.6471(8)	0.2760(3)	0.1702(2)	3.2(1)
C(2)′	0.7080(8)	0.3060(4)	0.2067(2)	3.2(2)
C(3)′	0.6760(8)	0.3832(4)	0.2212(2)	3.2(1)
C(4)′	0.5958(8)	0.4454(4)	0.2016(2)	3.1(1)
C(5)′	0.5001(8)	0.4317(4)	0.1685(2)	3.2(1)
C(6)′	0.8562(9)	0.3740(3)	0.1008(2)	3.4(1)
C(7)′	0.7931(8)	0.4515(3)	0.1027(2)	2.8(1)
C(8)′	0.8133(8)	0.5044(3)	0.1350(2)	2.9(1)
C(9)′	0.8881(8)	0.4906(3)	0.1719(2)	2.8(1)
C(10)′	0.9865(8)	0.4255(4)	0.1780(2)	3.1(1)
C(11)′	0.8299(9)	0.2595(4)	0.2296(2)	3.9(2)
C(12)′	0.6481(8)	0.5295(4)	0.2118(2)	3.4(1)
C(13)′	0.8248(8)	0.5378(4)	0.2076(2)	3.4(1)
C(14)′	0.6782(9)	0.4755(4)	0.0708(2)	3.6(2)

For the vanadium compound, the ESR spectrum (g = 1.982, A_v = 69.4 G) is generally similar to that for V(2,4-C_7H_{11})$_2$ (g = 1.974, A_v = 76.5 G), each having an eight-line pattern due to vanadium's nuclear spin of $^7/_2$. No obvious signs of line broadening were observed, which might have provided an indication for the presence of a second isomer. However, for the diamagnetic iron compound, NMR spectroscopic data provided a clear indication that two isomers were being formed. As can be seen in Figure 1, when first isolated, the crude and oily iron product displays two sets of resonances (each an eight-line pattern) in perhaps a 3:1 ratio. After sublimation, however, only the signals of one isomer remain, apparently due to the decomposition of the less stable isomer.[14] On the basis of spectroscopic[15] and theoretical arguments,[17] the more

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[14] Examination of a IIc/IIIc mixture by ^{1}H NMR spectroscopy as a function of time and heating indicated that both isomers were being lost by decomposition, the minor one faster than the major one.

[15] It can be noted that the positions of the terminal CH_2 group resonances in the ^{1}H NMR spectrum of the less stable isomer are not unlike those of Fe(2,4-C_7H_{11})$_2$, which has a conformation angle of 60°, whereas the corresponding positions for the more stable isomer are not unlike those of Ti(2,4-C_7H_{11})$_2$,[16] which has an expected conformation angle of 90°.

Table V. Pertinent Bond Distances (Å) and Angles (deg) for $Cr[4,4'-(CH_2)_2(2-C_6H_8)_2]$

Distances

Cr–C(1)	2.177(3)	Cr′–C(1)′	2.182(3)
Cr–C(2)	2.183(3)	Cr′–C(2)′	2.190(3)
Cr–C(3)	2.173(3)	Cr′–C(3)′	2.174(3)
Cr–C(4)	2.126(3)	Cr′–C(4)′	2.130(3)
Cr–C(5)	2.227(4)	Cr′–C(5)′	2.232(4)
Cr–C(6)	2.187(3)	Cr′–C(6)′	2.186(3)
Cr–C(7)	2.184(3)	Cr′–C(7)′	2.190(3)
Cr–C(8)	2.164(3)	Cr′–C(8)′	2.167(3)
Cr–C(9)	2.114(3)	Cr′–C(9)′	2.118(3)
Cr–C(10)	2.220(4)	Cr′–C(10)′	2.207(4)
C(1)–C(2)	1.427(4)	C(1)′–C(2)′	1.426(5)
C(2)–C(3)	1.417(5)	C(2)′–C(3)′	1.432(5)
C(2)–C(11)	1.514(5)	C(2)′–C(11)′	1.515(5)
C(3)–C(4)	1.435(5)	C(3)′–C(4)′	1.424(5)
C(4)–C(5)	1.374(5)	C(4)′–C(5)′	1.397(5)
C(4)–C(12)	1.548(5)	C(4)′–C(12)′	1.542(5)
C(6)–C(7)	1.433(4)	C(6)′–C(7)′	1.430(4)
C(7)–C(8)	1.428(4)	C(7)′–C(8)′	1.422(4)
C(7)–C(14)	1.500(5)	C(7)′–C(14)′	1.506(5)
C(8)–C(9)	1.411(4)	C(8)′–C(9)′	1.413(5)
C(9)–C(10)	1.408(5)	C(9)′–C(10)′	1.408(5)
C(9)–C(13)	1.540(5)	C(9)′–C(13)′	1.542(5)
C(12)–C(13)	1.517(5)	C(12)′–C(13)′	1.515(5)

Angles

C(1)–C(2)–C(3)	124.8(3)	C(1)′–C(2)′–C(3)′	123.7(3)
C(1)–C(2)–C(11)	118.3(3)	C(1)′–C(2)′–C(11)′	119.7(3)
C(3)–C(2)–C(11)	116.2(3)	C(3)′–C(2)′–C(11)′	116.1(3)
C(2)–C(3)–C(4)	127.6(3)	C(2)′–C(3)′–C(4)′	128.4(3)
C(3)–C(4)–C(5)	121.8(3)	C(3)′–C(4)′–C(5)′	121.4(3)
C(3)–C(4)–C(12)	115.5(3)	C(3)′–C(4)′–C(12)′	117.1(3)
C(5)–C(4)–C(12)	121.2(3)	C(5)′–C(4)′–C(12)′	120.0(3)
C(6)–C(7)–C(8)	125.1(3)	C(6)′–C(7)′–C(8)′	125.2(3)
C(6)–C(7)–C(14)	118.1(3)	C(6)′–C(7)′–C(14)′	117.7(3)
C(8)–C(7)–C(14)	116.2(3)	C(8)′–C(7)′–C(14)′	116.5(3)
C(7)–C(8)–C(9)	127.9(3)	C(7)′–C(8)′–C(9)′	128.1(3)
C(8)–C(9)–C(10)	122.0(3)	C(8)′–C(9)′–C(10)′	121.8(3)
C(8)–C(9)–C(13)	116.2(3)	C(8)′–C(9)′–C(13)′	116.0(3)
C(10)–C(9)–C(13)	120.2(3)	C(10)′–C(9)′–C(13)′	120.5(3)
C(4)–C(12)–C(13)	111.2(3)	C(4)′–C(12)′–C(13)′	110.7(3)
C(9)–C(13)–C(12)	111.2(3)	C(9)′–C(13)′–C(12)′	111.6(3)

stable isomer is presumed to be IIc, although a twist of perhaps 30° may occur, giving an approximate conformation angle near 90°.

Initial reaction studies indicate that the presence of the bridge can have a dramatic influence on the chemistry of these species. Whereas $Cr(2,4-C_7H_{11})_2$ has to date not yielded any ligand adducts, $Cr[4,4'-(CH_2)_2(2-C_6H_8)_2]$ reacts readily with CO to give a dicarbonyl, $Cr[4,4'-(CH_2)_2-\eta^5,\eta^{3'}-(2-C_6H_8)_2](CO)_2$, for which spectroscopic data (see Experimental Section) reveal that one dienyl ligand is bound to the metal in a η^3 fashion, and the other η^5, leading to an 18-electron configuration. With PF_3, an instant reaction is observed, leading to $Cr(PF_3)_6$, paralleling to some extent the "naked metal" reactions of $Cr(2,4-C_7H_{11})_2$. With bulkier alkylphosphines and alkyl phosphites, spectroscopic data indicate that 18-electron monoligand adducts are formed,[18] most likely as in IV, with both dienyl ligands retaining η^5 coordination. The formation of these adducts, however, is quite reversible, which has thus far precluded their isolation in pure form.

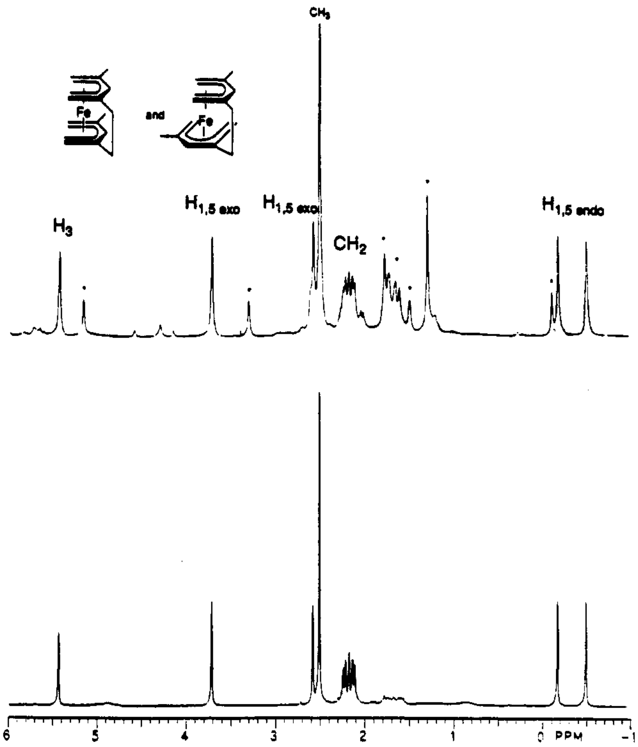
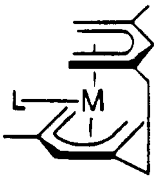


Figure 1. ^1H NMR spectra for $Fe[4,4'-(CH_2)_2(2-C_6H_8)_2]$: (top) as first isolated (peaks with asterisks are assigned to the less stable isomer); (bottom) after sublimation.



IV

A good degree of insight into the chemical differences may be obtained from structural data. The solid-state structure of the vanadium complex may be seen in Figure 2, while pertinent bonding parameters are contained in Tables II–III. First it may be seen that the complex lies on a crystallographic site of C_2 symmetry, like $Cr(2,4-C_7H_{11})_2$, but unlike $V(2,4-C_7H_{11})_2$. The bond distances and angles defined by the metal-bound carbon atoms are all as expected, based upon previous observations.[19] However, significant deviations from the expected do exist for other portions of the molecule. Thus, while the V–C(1,5), V–C(2,4), and V–C(3) bond lengths in $V(2,4-C_7H_{11})_2$ follow a regular pattern, averaging 2.179(4), 2.231(4), and 2.236(4) Å, resectively, those in the bridged complex are more irregular, particularly comparing V–C(2) with V–C(4), 2.252(1) vs 2.172(2) Å, respectively. Clearly, the bridge is responsible, apparently due to the large tilt of C(7) toward the vanadium atom, which also then pulls C(4) toward vanadium (vide infra).[20] Nonetheless, the

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(16) Liu, J.-Z.; Ernst, R. D. *J. Am. Chem. Soc.* 1982, *104*, 3737.

(17) Böhm, M. C.; Eckert-Maksić, M.; Ernst, R. D.; Wilson, D. R.; Gleiter, R. *J. Am. Chem. Soc.* 1982, *104*, 2699.

(18) For the $P(OCH_2)_3CCH_3$ (caution: highly toxic) complex, a parent ion peak could be observed in the 17-eV mass spectrum (*m/z* 389, 13% relative intensity), while no evidence of a free olefin bond could be found in either the IR or ^1H NMR spectrum. ^1H NMR (toluene-d_8): δ 4.52 (s, 2 H, H(3)), 3.66 (br s, 6 H, OCH_2), 2.7 (br m, 4 H, CH_2), 2.25 (br s, 2 H, H(1,5-exo)), 2.07 (br s, 2 H, H(1,5-exo)), 1.87 (s, 6 H, CH_3), 1.00 (s, 3 H, CH_3), 0.74 (br m, 2 H, H(1,5-endo)), 0.45 (br m, 2 H, H(1,5-endo)). At lower temperatures the CH_3 resonance at 1.87 ppm undergoes decoalescence, and thus the structure is unsymmetric.

(19) (a) Ernst, R. D. *Struct. Bonding (Berlin)* 1984, *57*, 1. (b) Ernst, R. D. *Chem. Rev.* 1988, *88*, 1255.

(20) It can also be observed that the terminal CH_2 group adjacent to the bridged carbon atom is further from the metal than the other CH_2 group. Apparently, as one moves further from the bridged position, the open dienyl ligand is able to twist itself closer to the metal atom.

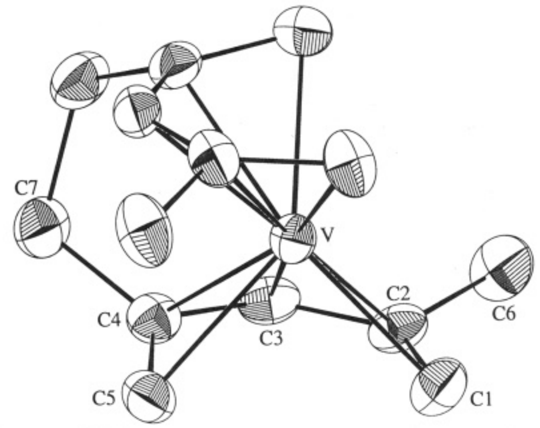

Figure 2. Solid-state structure of $V[4,4'\text{-}(CH_2)_2(2\text{-}C_6H_8)_2]$.

overall average[21] V–C bond distance is similar to that in $V(2,4\text{-}C_7H_{11})_2$, 2.215(1) vs 2.211(2) Å, respectively. The conformation angles,[22] relative to the 0° value for the syn-eclipsed structure (V), are also similar at 90.6 vs 89.8°, respectively.

V

The deviation of C(7) from the dienyl plane is especially notable. For comparison, the deviation of C(6), 0.147 Å toward the metal atom, translates to a tilt of 4.6°, which is rather normal.[23] The much larger deformation of C(7), 0.674 Å or 26.2°, is clearly far from normal and readily explains some of the previously discussed anomalies. The reason for this severe deformation can be traced to the girth of the metal-bound carbon atoms in a pentadienyl ligand. With a typical separation between terminal carbon atoms of ca. 3 Å (cf., ca. 1.4 Å for C_5H_5), pentadienyl ligand planes must make closer approaches to their attached metal atoms, in this case 1.542 Å, for them to have reasonable M–C bond distances. The structural picture (Figure 3) makes it clear that an unstrained C_2H_4-bridged dipentadienyl ligand is not able to chelate a first row transition metal effectively. Instead, the dienyl planes must tilt toward each other, thereby giving rise to the observed deformation. In fact, in a related complex of the much larger Yb(II) ion,[5] there is almost no distortion of this type (9.5° for the CH_2 tilt vs 4.9° for the CH_3 tilt), whereas in progressively smaller transition metal ions (Cr, Fe), even greater deformations must take place, which readily accounts for the reverse order of stability for these bridged open metallocenes.

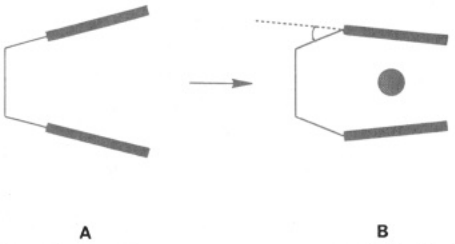

Figure 3. Approximate structures of $M[4,4'\text{-}(CH_2)_2(2\text{-}C_6H_8)_2]$ complexes: (a) undistorted, poor interaction with metal; (b) distorted, better interaction with metal.

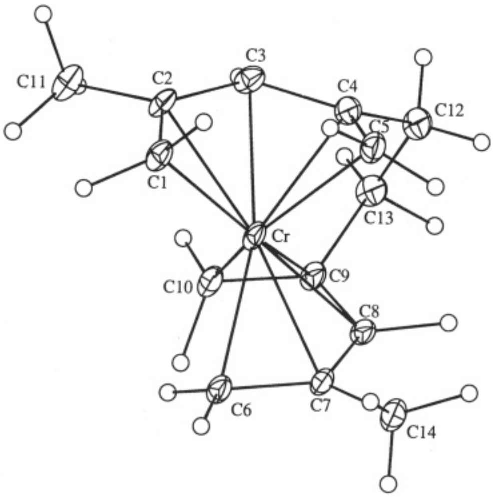

Figure 4. Solid-state structure of $Cr[4,4'\text{-}(CH_2)_2(2\text{-}C_6H_8)_2]$.

The structure of the bridged open chromocene complex has also been determined (Figure 4) and is generally consistent with the previous observations. Two independent molecules are found in the unit cell, and overall they are essentially identical. Once again, the bonding parameters for the ligand fragments are generally normal. The metal–carbon bonds are not nearly as regular as those in the open metallocene, $Cr(2,4\text{-}C_7H_{11})_2$, for which all bonds were reasonably equivalent at 2.163(3) Å. For IIb, the average Cr–C distance is 2.176(2) Å, with the average Cr–C(1–5) bond lengths for the two molecules being 2.183(2), 2.187(2), 2.170(2), 2.122(2), and 2.221(2) Å, respectively. Analogous to the vanadium complex, the C(4) atoms are drawn closer to the metal by the tilt of their attached CH_2 groups toward the metal. As would be expected for the smaller metal size, a greater deformation of the CH_2 groups below the dienyl plane is necessary to lead to a relatively effective interaction with the metal center. In this case, the CH_2 deformations range from 0.73 to 0.75 Å, equaling an average of 28.5°. For comparison, the methyl group deformations average 5.6°. The average deviation of the chromium atoms from the dienyl ligand planes is 1.538 Å. Interestingly, the conformation angle for this complex is 92.2°, actually greater than that of 90.6° in the corresponding vanadium complex, whereas in the $M(2,4\text{-}C_7H_{11})_2$ series (M = V, Cr, Fe), a clear trend in the opposite direction was observed (89.8, 82.3, and 59.7°). It seems possible that for the bridged chromium complex the greater deformations of the two dienyl ligands, relative to the bridged vanadium analog, may work to hinder the twisting of the two dienyl planes from the ideal 120° conformation angle of IIb.

It appears that the introduction of a bridge between two pentadienyl ligands leads to an even greater alteration of the chemistry relative to bridged bis(cyclopentadienyl) ligands. The bridged open metallocenes display significantly different trends in thermal stabilities, air sensi-

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[21] The esd's quoted for averaged values are derived solely from the esd's of the individual values making up the average. As such, these esd's reflect the uncertainties in the average values, but not the distributions of the individual values.

[22] The conformation angles are defined as the angles between the two $M\text{–}C(3)\text{–}{}^1/_2(C(1)+C(5))$ planes for a given molecule, with a syn-eclipsed conformation being 0°, anti-eclipsed being 180°.

[23] The substituent tilts in angstroms are estimated by the deviation of the substituent from the given C(1)–C(5) plane. The sine of the tilt angle is defined as this deviation divided by the bond length between the substituent and the dienyl carbon atom to which it is attached.

tivities, and chemical reactivities relative to the unbridged open metallocenes, and these trends all seem related to the significant distortion that must occur for the bridging ligands to chelate a relatively small metal center. It is thus no surprise that the iron complex should be so unstable. It does seem a bit of a surprise, however, that to date a titanium analog could not be isolated, as Ti$(2,4\text{-}C_7H_{11})_2$ is quite stable thermally and the larger Ti(II) center should be better accommodated by the bridged bis(pentadienyl) ligands. Hopefully, an explanation for this situation will be forthcoming.

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Supplementary Material Available: Diagrams of the Mn_3 compound and tables of positional and anisotropic thermal parameters for the structural determinations, least-squares planes, structural data, and bond distances and angles for the unknown $M_3[4,4'\text{-}(CH_2)_2(2\text{-}C_6H_8)_2]_2$ (38 pages). Ordering information is given on any current masthead page.

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