Structural and Reaction Chemistry of the "Open Chromocene" Bis(2,4-dimethylpentadienyl)chromium

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The reactivity of the "open chromocene" $Cr(2,4\text{-}C_7H_{11})_2$ (C_7H_{11} = dimethylpentadienyl) has been investigated and found to parallel that of metal allyl complexes, such as $Ni(C_3H_5)_2$. Thus, exposure to an excess of dmpe ($Me_2PC_2H_4PMe_2$) or $t\text{-}C_4H_9NC$ brings about "naked chromium reactions", leading to the formation of $Cr(dmpe)_3$ and $Cr(CN(t\text{-}C_4H_9))_6$, respectively, in good yields. With amine hydrochlorides and dmpe, one pentadienyl ligand may be removed, leading to the paramagnetic, 16-electron complex $Cr(2,4\text{-}C_7H_{11})(Cl)(dmpe)$, which could also be prepared from $CrCl_2(dmpe)_2$ and 1 equiv of $K(2,4\text{-}C_7H_{11})$. Reaction of the monochloride complex with $LiCH_3$ leads to the formation of the analogous methyl complex. Structural determinations are reported for $Cr(2,4\text{-}C_7H_{11})_2$ and $Cr(2,4\text{-}C_7H_{11})(Cl)(dmpe)$. For $Cr(2,4\text{-}C_7H_{11})_2$, an open-sandwich structure was found, with the average Cr–C bond distance being 2.163 (3) Å, comparable to the value of 2.169 (4) Å for chromocene. The structure has been refined to agreement indices of R = 0.040 and R_w = 0.053 in space group D_4^4—$P4_32_12$ (No. 96) with $a = b$ = 8.090 (1) Å and c = 20.847 (3) Å for Z = 4. For $Cr(2,4\text{-}C_7H_{11})(Cl)(dmpe)$, an unsymmetric "piano-stool" geometry was observed, in which one phosphorus atom is located under the open edge of the pentadienyl ligand, while the chlorine atom and other phosphorus atom are located under the formally uncharged C(2) and C(4) atoms of the pentadienyl ligand. The structure has been refined to agreement indices of R = 0.063 and R_w = 0.056 in space group D_{2h}^{15}—$Pbca$ (No. 61) with a = 12.578 (2) Å, b = 12.117 (2) Å, and c = 23.094 (5) Å for Z = 8.

We have previously demonstrated that a wide variety of thermally stable homoleptic metal pentadienyl compounds may be prepared[2] and that these species are characterized by interesting bonding and conformational natures.[2] Several considerations have indicated that such compounds should also possess high chemical and catalytic reactivities. Indeed, reactions have been observed in which metal pentadienyl compounds, even the "open ferrocenes", engage in coupling, "naked metal", isomerization, and polymerization processes.[3] We have extended our studies now to include representative reactions of the "open chromocene" $Cr(2,4\text{-}C_7H_{11})_2$ (C_7H_{11} = dimethylpentadienyl), and our observations are reported herein.

Experimental Section

All operations involving organometallics were carried out under a nitrogen atmosphere in prepurified Schlenk apparatus or in a glovebox. Nonaqueous solvents were thoroughly dried and deoxygenated in a manner appropriate to each and were distilled immediately before use. Elemental analyses were performed by MicAnal Laboratories.

Spectroscopic Studies. Infrared spectra were recorded with a Perkin-Elmer 298 spectrophotometer. Mulls were prepared in a glovebox with dry, degassed Nujol. ^1H and ^{13}C nuclear magnetic resonance spectra were recorded in toluene-d_8 on Varian EM-390, SC-300, and XL-300 spectrometers. Mass spectra (17 or 70 eV) were performed on a VG Micromass 7070 double-focusing high-resolution mass spectrometer with VG Data System 2000. Except for the parent fragment, peaks are only quoted if their relative intensities are at least 10% of the intensity of the strongest peak.

Reaction of $Cr(2,4\text{-}C_7H_{11})_2$ with $(CH_3)_2PC_2H_4P(CH_3)_2$ (dmpe). Bis(2,4-dimethylpentadienyl)chromium[4] (0.50 g, 2.06 mmol) and bis(dimethylphosphino)ethane[5] (1.86 g, 12.4 mmol) in 20 mL of THF were refluxed under nitrogen for 30 h. The solution was then allowed to cool and the supernatant removed, leaving behind the bright yellow product (mp 290 °C dec), which was then recrystallized from toluene and isolated in 58% yield (0.60 g). The product was identified as $Cr(dmpe)_3$[6] by melting point and spectral data. Infrared data (Nujol mull): 1412 (m), 1281 (s), 1258 (m), 1109 (w), 1051 (w), 910 (vs), 887 (sh), 869 (s), 816 (m), 777 (m), 669 (s), 652 (s), 610 (vs). Mass spectrum: *m/e* (relative intensity): 61 (18), 62 (11), 107 (84), 122 (100), 135 (71), 202 (1), 352 (1).

Reaction of $Cr(2,4\text{-}C_7H_{11})_2$ with $t\text{-}C_4H_9NC$. To a stirred solution of 0.50 g (2.1 mmol) of bis(2,4-dimethylpentadienyl)chromium in 50 mL of THF at −78 °C was added 1.40 mL (12.4 mmol) of *tert*-butyl isocyanide by syringe. The solution was allowed to warm slowly to ambient temperature and allowed to complete reaction over the course of 12 h, resulting in a color change from emerald-green to orange-yellow. The solvent and excess *tert*-butyl isocyanide was removed in vacuo and the residue extracted with three 30-mL portions of hexane. The solution was filtered, concentrated, and cooled to −30 °C, yielding 0.77 g (68%) of crystalline orange-red product. ^1H NMR, IR, and melting point data were essentially identical with those reported for $Cr(CN(t\text{-}C_4H_9))_6$.[7] Anal. Calcd for $CrC_{30}H_{54}N_6$: C, 65.42; H, 9.88; N, 15.26. Found: C, 65.88; H, 10.16; N, 15.05. A similar reaction utilizing C_6H_5NC yielded the corresponding $Cr(CNC_6H_5)_6$ complex.

Reaction of $Cr(2,4\text{-}C_7H_{11})_2$ with dmpe and Solid CH_3NH_3Cl. Anhydrous CH_3NH_3Cl (0.087 g, 1.3 mmol) was added to a stirred solution of bis(2,4-dimethylpentadienyl)chromium (0.31 g, 1.3 mmol) and dmpe (0.21 g, 1.5 mmol) in 20 mL of THF at −78 °C. The reaction mixture was allowed to warm slowly to room temperature with stirring overnight, after which the solvent was removed in vacuo and the residue extracted into warm hexanes and filtered through Celite. The volume of the hexane solution

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was reduced to ca. 20 mL and stored overnight at −20 °C, after which 0.05 g (18%) of yellow-green crystals were isolated, identified by IR as *trans*-$CrCl_2(dmpe)_2$.[8] Solvent was removed in vacuo from the remaining supernatant, and unreacted $Cr(2,4\text{-}C_7H_{11})_2$ (0.25 g, 80%) was sublimed away from red-brown $Cr(dmpe)(Cl)(2,4\text{-}C_7H_{11})$ (ca. 0.5 mg, 1%) identified by IR.

Chloro(η^5-2,4-dimethylpentadienyl)(bis(dimethylphosphino)ethane)chromium, $Cr(\eta^5\text{-}2,4\text{-}(CH_3)_2C_5H_5)(Cl)(dmpe)$. A slurry of $(i\text{-}Pr)_2NH_2Cl$ (0.19 g, 1.4 mmol) in 15 mL of THF was added dropwise to a stirred solution of $Cr(2,4\text{-}C_7H_{11})_2$ (0.34 g, 1.4 mmol) and dmpe (0.21 g, 1.4 mmol) in 25 mL of hexanes at −78 °C. The solution was allowed to warm to room temperature while being stirred overnight, after which the solvent was removed in vacuo and the residue extracted into warm hexanes and filtered through Celite. The volume of the hexane solution was reduced to ca. 8 mL, whereupon cooling to −90 °C overnight led to the isolation of red-brown crystals of $Cr(2,4\text{-}C_7H_{11})(Cl)(dmpe)$ (0.06 g, 13%). No $CrCl_2(dmpe)_2$ was detected. Anal. Calcd for $C_{13}H_{27}ClP_2Cr$: C, 46.92; H, 8.18. Found: C, 46.78, H, 8.34.

Alternatively, a solution containing $K(2,4\text{-}(CH_3)_2C_5H_5)$ (0.64 g, 4.8 mmol) in 15 mL of THF was added dropwise to a stirred solution of $CrCl_2(dmpe)_2$ (2.00 g, 4.7 mmol) in 20 mL of THF cooled to −78 °C. The reaction mixture was allowed to warm to room temperature over a 2–4 h period and then stirred for an additional 2 h. The solvent was removed in vacuo and the red-brown product extracted into hot hexanes. The solution was filtered through Celite and concentrated to ca. 20 mL whereupon cooling to −20 °C afforded 1.26 g (80%) of dark brown crystals (mp 154–155 °C). Anal. Calcd for $C_{13}H_{27}ClP_2Cr$: C, 46.92; H, 8.18; Cl, 10.66. Found: C, 47.13; H, 8.46; Cl, 10.86.

Infrared data (Nujol mull): 3065 (w), 3045 (w), 3025 (w), 1415 (s), 1299 (m), 1282 (ms), 1128 (w), 1083 (w), 1020 (w), 1000 (w), 987 (w), 976 (w), 945 (vs), 928 (vs), 897 (ms), 878 (m), 859 (m), 853 (m), 837 (m), 787 (w), 739 (ms), 734 (ms), 706 (s), 648 (ms). Magnetic susceptibility (Evans method): 2.7 μ_B. Mass spectrum: *m/e* (relative intensity): 55 (15), 62 (19), 67 (16), 79 (14), 81 (14), 91 (22), 92 (55), 95 (35), 107 (53), 122 (100), 135 (75), 237 (12), 332 (5), 334 (2).

Methyl(η^5-2,4-dimethylpentadienyl)(bis(dimethylphosphino)ethane)chromium, $Cr(\eta^5\text{-}2,4\text{-}(CH_3)_2C_5H_5)CH_3(dmpe)$. A hexane solution of CH_3Li (2.5 mL of 1.2 M, 3.0 mmol) was added dropwise to a stirred solution of 0.86 g (2.6 mmol) of $Cr(\eta^5\text{-}2,4\text{-}(CH_3)_2C_5H_5)Cl(dmpe)$ in 25 mL of ethyl ether at −78 °C. The mixture was allowed to warm to room temperature over ca. 3 h, and stirring was continued for an additional 2 h, after which the solvent was removed in vacuo and the residue extracted into hexanes and filtered through Celite. After the volume was reduced to ca. 10 mL, the solution was stored overnight at −20 °C leading to crystallization of the yellow-brown product (mp 135–140 °C), which was isolated in a 60% yield (0.48 g). Anal. Calcd for $C_{14}H_{30}P_2Cr$: C, 53.35; H, 9.98. Found: C, 53.84; H, 9.68; Cl, <0.05.

Infrared data (Nujol mull): 3065 (m), 3038 (m), 3018 (m), 2788 (m), 1412 (s), 1293 (m), 1279 (m), 1262 (w), 1125 (m), 1076 (w), 1018 (w), 999 (w), 987 (w), 937 (vs), 922 (vs), 910 (sh), 890 (s), 860 (sh), 848 (m), 832 (m), 810 (w), 785 (w), 732 (m), 725 (m), 698 (s), 643 (s), 616 (w). Magnetic susceptibility (Evans method, THF): 2.3 μ_B. Mass spectrum: *m/e* (relative intensity) 41(15), 62 (11), 79 (11), 95 (16), 107 (69), 122 (100), 135 (77), 174 (10), 202 (36), 297 (39), 312 (16).

X-ray Diffraction Studies of $Cr(2,4\text{-}C_7H_{11})_2$ and $Cr(2,4\text{-}C_7H_{11})(Cl)(dmpe)$. Single crystals of these compounds were grown by slowly cooling saturated solutions in pentane and hexane/toluene, respectively. These were subsequently mounted under nitrogen in sealed glass capillaries and transferred to a Nicolet P$\bar{1}$ autodiffractometer at the University of Utah. Unit cell constants and preliminary space group assignments were obtained from a combination of oscillation photographs, standard software programs, and observed extinctions. Further confirmation was achieved through cell reduction. Data were subsequently collected as described in Table I using Mo Kα radiation (λ = 0.7107 Å). Space group $P4_32_12$ could be unambiguously chosen over $P4_12_12$ through conventional refinements (those for the latter configuration yielded agreement indices consistently higher by 0.005) and through the η refinement method.[9]

Table I. X-ray Data Parameters for $Cr(2,4\text{-}C_7H_{11})_2$ and $Cr(2,4\text{-}C_7H_{11})(dmpe)Cl$

	$Cr(2,4\text{-}C_7H_{11})_2$	$Cr(2,4\text{-}C_7H_{11})(dmpe)Cl$
formula	$C_{14}H_{22}Cr$	$C_{13}H_{27}ClCrP_2$
mol wt	242.23	332.75
space group	$P4_32_12$	Pbca
lattice constants		
a, Å	8.090 (1)	12.578 (2)
b, Å	8.090 (1)	12.117 (2)
c, Å	20.847 (3)	23.094 (5)
V, Å^3	1364.4 (3)	3519.5 (11)
Z	4	8
d(calcd), g cm^{-1}	1.18	1.26
radiation	Mo Kα	Mo Kα
temp, °C	25	25
cryst shape	multifaceted polygon	multifaceted polygon
linear abs coeff, cm^{-1}	7.88	9.49
scan type	θ–2θ	θ–2θ
scan speed, deg min^{-1}	1.0	2.0–3.0
bkgd treatment	0.5(scan time)	CARESS[a]
scan range, deg	Kα_1 − 1.45, Kα_2 + 0.85	Kα_1 − 1.00, Kα_2 + 1.00
2θ limits, deg	$3° \leq 2\theta \leq 40°$	$3° \leq 2\theta \leq 50°$
data collected	841	3641
no. of unique data	791	3527
unique data with $I > 3\sigma(I)$	589	1961
R(*F*)	0.040	0.063
$R_w(F)$	0.053	0.056
max diff Fourier peak, e/Å^3	0.35	1.05

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Heavy atom (Cr, P, Cl) positions in each case were readily found through direct methods. Ensuing difference Fourier maps led to the location of the carbon atoms. For $Cr(2,4\text{-}C_7H_{11})_2$, methyl group hydrogen atoms were subsequently placed in idealized positions, with *d*(C–H) = 0.96 Å, while the other hydrogen atom positions were refined. All of these were assigned isotropic thermal parameters of *U* = 0.06. For $Cr(2,4\text{-}C_7H_{11})(Cl)(dmpe)$, all hydrogen atoms were placed in locations suggested by a difference Fourier map and subjected to isotropic refinement. Calculations for $Cr(2,4\text{-}C_7H_{11})_2$ were carried out at Nicolet Instrument Corp. using the SHELX programs, while for $Cr(2,4\text{-}C_7H_{11})(Cl)(dmpe)$, Strouse's programs were utilized at the University of Utah.

Synthetic Results and Discussion

Little has previously been known concerning the reactivity of "open chromocenes" such as $Cr(2,4\text{-}C_7H_{11})_2$.[10] While its titanium and vanadium analogues readily form adducts with CO[11,12] and PF_3,[12] $Cr(2,4\text{-}C_7H_{11})_2$ undergoes no such reactions,[12] even though chromocene itself does form a weakly bound carbonyl adduct.[13] Nonetheless, we have now found that longer exposure of $Cr(2,4\text{-}C_7H_{11})_2$ to 1,2-bis(dimethylphosphino)ethane, dmpe, in refluxing THF leads to the formation of $Cr(dmpe)_3$ in 58% isolated

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[10] (a) Prolonged exposure of $Cr(C_5H_7)_2$ to CO has been reported to lead to $Cr(CO)_6$.[10b] (b) Giannini, U.; Pellino, E.; Lachi, M. P. *J. Organomet. Chem.* **1968**, *12*, 551.

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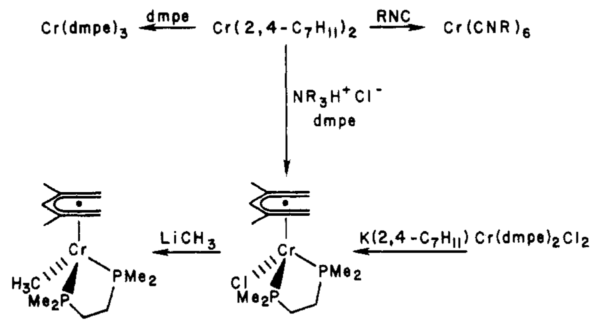
Scheme I



yield. This can be compared to a reported yield of 25% from the reduction of $CrCl_3(THF)_3$ in the presence of dmpe,[6] or ca. 50% (based on metal) from a metal atom reaction,[14] which actually required a significant excess of dmpe. Hence, the present procedure represents a useful alternative synthesis of Cr(dmpe)$_3$. Similar results were obtained in reactions of Cr(2,4-C_7H_{11})$_2$ with isocyanides. Cr(2,4-C_7H_{11})$_2$ was found to react readily at room temperature with *t*-C_4H_9NC yielding the known Cr(*t*-C_4H_9NC)$_6$[7] in an isolated yield of ca. 68%. The known $Cr(C_6H_5NC)_6$[15] could similarly be obtained from Cr(2,4-C_7H_{11})$_2$ and excess C_6H_5NC. For at least the dmpe reactions, the fate of the pentadienyl ligands appears to be nearly exclusively dimerization, and hydrogen atom abstraction products such as 2,4-dimethyl-1,3-pentadiene seemed virtually absent. Hence, it is clear that Cr(2,4-C_7H_{11})$_2$ readily participates in "bare" or "naked-metal" reactions, quite reminiscent of $Ni(C_3H_5)_2$.[16]

Similar to the behavior of allyl ligands in complexes such as $Cr(C_3H_5)_3$,[17] $Co(C_3H_5)_3$,[17] $Ni(C_3H_5)_2$,[16] and $U(C_3H_5)_4$,[18] a pentadienyl ligand may be selectively removed from Cr(2,4-C_7H_{11})$_2$ on treatment with an equivalent of HCl (via *i*-$Pr_2NH_2^+Cl^-$) in hexane. However, compared to the loss of an allyl ligand, the loss of a pentadienyl ligand brings about a greater reduction in the metal atom's electron count, and therefore a supplemental chelating ligand, dmpe, was introduced to compensate for this loss. Under these conditions, the complex Cr(2,4-C_7H_{11})(Cl)(dmpe) could be isolated (Scheme I), although in low yield (13%). An alternative route, involving the reaction of $CrCl_2$(dmpe)$_2$ with 1 equiv of the 2,4-dimethylpentadienyl anion, was found to proceed selectively, with yields of 80% being attainable. Analogous to the 16-electron Cr(2,4-C_7H_{11})$_2$ complex, Cr(2,4-C_7H_{11})(Cl)(dmpe) also possesses two unpaired electrons. The chloride ligand in Cr(2,4-C_7H_{11})(Cl)(dmpe) was found to be replaceable, and a reaction with $LiCH_3$ led to the likewise paramagnetic Cr(2,4-C_7H_{11})(CH_3)(dmpe) complex.

Crystallographic Results and Discussion

The result of the structural determination of Cr(2,4-C_7H_{11})$_2$ may be seen in Figure 1. Pertinent positional and bonding parameters may be found in Tables II and III, while thermal parameters, least-squares plane information, and structure factor tables are available as supplementary material. The molecule was found to possess crystallographically imposed C_2 symmetry. The Cr–C bond distances average[19] 2.163 (3) Å, quite similar to the value of 2.169 (4) Å for chromocene itself.[20] Notable is the fact that the various Cr–C bond distances are reasonably similar, whereas in V(2,4-C_7H_{11})$_2$ the M–C(1,5) bonds were noticeably shorter than the rest,[21] while for Fe(2,4-C_7H_{11})$_2$, they were the longest.[22]

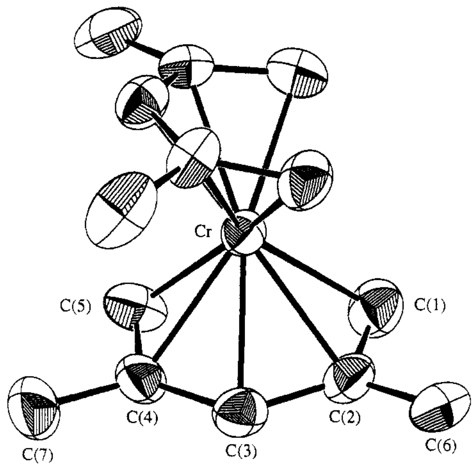


Figure 1. Perspective view and numbering scheme for Cr(2,4-C_7H_{11})$_2$. The molecule lies on a twofold rotation axis.

Table II. Positional Coordinates for the Refined Atoms of Cr(2,4-C_7H_{11})$_2$

atom	*x*	*y*	*z*
Cr	0.44281 (10)	0.44281 (10)	0.00000 (0)
C(1)	0.6208 (9)	0.5319 (10)	0.0682 (3)
C(2)	0.4906 (8)	0.4638 (8)	0.1014 (3)
C(3)	0.4284 (10)	0.3054 (9)	0.0889 (3)
C(4)	0.4687 (9)	0.1945 (7)	0.0403 (3)
C(5)	0.5939 (9)	0.2224 (9)	-0.0031 (4)
C(6)	0.3983 (9)	0.5744 (9)	0.1475 (3)
C(7)	0.3559 (11)	0.0492 (9)	0.0285 (4)
H(1A)	0.709 (5)	0.476 (5)	0.057 (2)
H(1B)	0.633 (7)	0.639 (3)	0.073 (2)
H(3)	0.330 (4)	0.292 (7)	0.105 (2)
H(5A)	0.689 (4)	0.263 (6)	0.009 (3)
H(5B)	0.615 (7)	0.159 (6)	-0.036 (2)

Table III. Pertinent Bonding Parameters for Cr(2,4-C_7H_{11})$_2$

Bond Distances (Å)			
Cr-C(1)	2.148 (7)	C(1)-C(2)	1.375 (10)
Cr-C(2)	2.155 (5)	C(2)-C(3)	1.401 (10)
Cr-C(3)	2.163 (6)	C(3)-C(4)	1.391 (9)
Cr-C(4)	2.188 (6)	C(4)-C(5)	1.378 (10)
Cr-C(5)	2.163 (7)	C(2)-C(6)	1.511 (9)
		C(4)-C(7)	1.508 (10)
Bond Angles (deg)			
C(1)-C(2)-C(3)	123.2 (6)	C(3)-C(4)-C(5)	123.0 (6)
C(1)-C(2)-C(6)	117.5 (6)	C(3)-C(4)-C(7)	118.6 (6)
C(2)-C(3)-C(4)	129.9 (6)	C(5)-C(4)-C(7)	117.7 (6)
C(3)-C(2)-C(6)	118.8 (6)		

The pentadienyl ligands, based on the five metal-bound carbon atoms, are reasonably planar. The methyl groups

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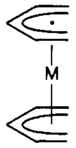
assume an average bend of 10.8° toward the metal atom,[23] apparently in an attempt to improve the orbital overlap between the metal and the pentadienyl system.[20b] The chromium atom is located 1.520 Å from this plane, which can be compared to the 1.599 (3) Å distance between the chromium atom and the center of mass of the five metal-bound carbon atoms. For chromocene, there is no distinction between these two parameters, which equal 1.798 Å. The much shorter values for $Cr(2,4\text{-}C_7H_{11})_2$ are indicative of the greater steric crowding brought about by pentadienyl ligands compared to cyclopentadienyl (cone angles = ca. 180° vs 136°).[24]

The delocalized carbon–carbon bond distances average 1.386 (5) Å, while the C–CH_3 distances average 1.510 (7) Å. As is generally the case, the C-C-C angles about a methylated carbon atom are smaller than those not having an attached methyl group.[25] Thus, $\angle$C(2)–C(3)–C(4) = 129.9 (6)° vs an average of 123.1 (4)° for $\angle$C(1)–C(2)–C(3) and C(3)–C(4)–C(5). It can be noted that in the $M(2,4\text{-}C_7H_{11})_2$ (M = V, Cr, Fe) series, these angles tend to sequentially decrease, as can be observed by the decreasing C(1)–C(5) separations of 3.05 (1), 2.92 (2), and 2.785 (5) Å, respectively.[21,22,26] As the ligand becomes smaller for the smaller metal, one can attribute this to an attempt for the large ligand to optimize overlap with the smaller metals, and a similar correlation has been drawn for the allyl ligand.[26] The relative orientations of the two pentadienyl ligands are also of interest. First, the two ligand planes are tilted 19.4° relative to one another, such that the pentadienyl plane is furthest from the opposing C(4) atom, followed by C(3), C(5), C(2), and C(1). A second parameter involves the relative twist existing between the two ligand planes. In order to specify the degree of twists of the ligands from the syn-eclipsed I to the anti-eclipsed II conformation, a plane for each ligand can be constructed, involving the metal atom, the C(3) atom, and the midpoint between the C(1) and C(5) atoms. With such a definition, $Fe(2,4\text{-}C_7H_{11})_2$ has been found to possess a conformation angle, χ, of 59.7°, very close to the ideal value of 60° for the gauche-eclipsed conformation III.[22] For $V(2,4\text{-}C_7H_{11})_2$, an angle of 89.8° was found, very close to the value of 90° for an ideally staggered conformation IV.[21] For $Cr(2,4\text{-}C_7H_{11})_2$, the value of χ has been found to be 82.2°, intermediate between the vanadium and iron values. Actually, due to the fact that the pentadienyl C–C–C bond angles exceed 120°, the chromium complex is actually the one which is closest to being staggered. Thus, the true staggered conformation should be reached not at 90°, but at 90 - $^1/_2$[$\angle$C(1)–C(2)–C(3) + $\angle$C(2)–C(3)–C(4) + $\angle$(C(3)–C(4)–C(5) - 360°]. For $Cr(2,4\text{-}C_7H_{11})_2$, this value would be 82°, and at this value the C(3)–$^1/_2$(C(1) + C(5)) vector would still be directed toward the midpoint of the other ligand's C(1)–C(2) bond, if minor differences in C–C bond distances are ignored.



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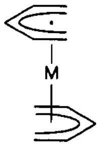

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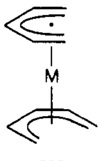

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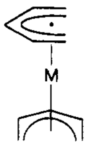

IV

It is interesting that both the conformations and the trends in relative M–C bond distances may be correlated with δ-bonding arguments. It has already been found that δ (Fe$\rightarrow$pentadienyl) bonding is quite significant for the "open ferrocenes"[27] and might therefore be responsible for the trend in conformation from staggered (Ti, V) to eclipsed (Fe). In addition, one can note that such δ bonding should be more important for the formally uncharged C(2,4) atoms, while the π (pentadienyl$\rightarrow$M) interaction

Table IV. Positional Parameters for the Non-Hydrogen Atoms of $Cr(2,4\text{-}C_7H_{11})(dmpe)(Cl)$

atom	*x*	*y*	*z*
Cr	0.48703 (7)	0.24004 (7)	0.61131 (4)
Cl	0.40269 (13)	0.36117 (14)	0.67644 (7)
P(1)	0.31600 (12)	0.14320 (13)	0.61152 (7)
P(2)	0.52540 (13)	0.11099 (14)	0.68440 (7)
C(1)	0.6508 (5)	0.2920 (7)	0.6218 (3)
C(2)	0.5975 (6)	0.3673 (6)	0.5847 (3)
C(3)	0.5366 (6)	0.3361 (6)	0.5365 (3)
C(4)	0.5086 (6)	0.2277 (6)	0.5189 (3)
C(5)	0.5493 (6)	0.1323 (7)	0.5462 (4)
C(6)	0.5930 (8)	0.4886 (7)	0.6025 (4)
C(7)	0.4251 (8)	0.2184 (9)	0.4707 (4)
C(8)	0.1926 (6)	0.2219 (7)	0.6076 (4)
C(9)	0.2854 (8)	0.0270 (7)	0.5633 (3)
C(10)	0.3092 (6)	0.0753 (6)	0.6830 (3)
C(11)	0.4139 (6)	0.0150 (6)	0.6936 (3)
C(12)	0.6388 (7)	0.0196 (8)	0.6776 (4)
C(13)	0.5424 (7)	0.1666 (8)	0.7569 (4)

Table V. Hydrogen Atom Parameters for $Cr(2,4\text{-}C_7H_{11})(dmpe)(Cl)$

atom	*x*	*y*	*z*	*U*
H(11)	0.694 (6)	0.236 (7)	0.607 (3)	0.059
H(12)	0.686 (6)	0.329 (6)	0.656 (3)	0.059
H(31)	0.503 (6)	0.395 (6)	0.514 (3)	0.056
H(51)	0.520 (6)	0.066 (6)	0.536 (3)	0.053
H(52)	0.627 (6)	0.125 (6)	0.550 (3)	0.053
H(61)	0.642 (7)	0.537 (8)	0.582 (4)	0.077
H(62)	0.538 (7)	0.528 (8)	0.586 (4)	0.077
H(63)	0.593 (7)	0.483 (7)	0.644 (4)	0.077
H(71)	0.448 (7)	0.222 (8)	0.438 (4)	0.082
H(72)	0.388 (7)	0.140 (7)	0.476 (4)	0.082
H(73)	0.367 (7)	0.272 (7)	0.475 (4)	0.082
H(81)	0.141 (6)	0.168 (6)	0.609 (3)	0.058
H(82)	0.195 (6)	0.262 (7)	0.574 (3)	0.058
H(83)	0.189 (7)	0.262 (7)	0.635 (3)	0.058
H(91)	0.279 (7)	0.053 (7)	0.532 (3)	0.058
H(92)	0.347 (6)	−0.026 (6)	0.560 (3)	0.058
H(93)	0.226 (6)	−0.004 (6)	0.580 (3)	0.058
H(101)	0.248 (6)	0.034 (6)	0.686 (3)	0.052
H(102)	0.306 (7)	0.117 (7)	0.707 (3)	0.052
H(111)	0.421 (7)	−0.041 (6)	0.668 (3)	0.059
H(112)	0.416 (7)	−0.028 (6)	0.727 (3)	0.059
H(121)	0.701 (7)	0.065 (7)	0.673 (4)	0.071
H(122)	0.639 (7)	−0.038 (7)	0.706 (4)	0.071
H(123)	0.631 (7)	−0.019 (7)	0.643 (4)	0.071
H(131)	0.604 (6)	0.216 (6)	0.761 (3)	0.063
H(132)	0.481 (6)	0.193 (7)	0.762 (4)	0.063
H(133)	0.554 (7)	0.118 (7)	0.784 (3)	0.063

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[23] The exo hydrogen atoms on C(1) and C(5) experience a similar distortion of ca. 11°, while for H(3) the value is 16°. The endo hydrogen atoms on C(1) and C(5) bend away from the metal by an average of 38°. The hydrogen atom refinement was constrained so that all C–H distances would be equivalent. The final C–H distance was 0.87 (2) Å.

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Table VI. Pertinent Bonding Parameters for $Cr(2,4\text{-}C_7H_{11})(dmpe)(Cl)$

		Bond Distance (Å)			
Cr–C(1)	2.168 (7)	Cr–Cl	2.354 (2)	P(1)–C(8)	1.824 (7)
Cr–C(2)	2.164 (7)	C(1)–C(2)	1.420 (10)	P(1)–C(9)	1.836 (8)
Cr–C(3)	2.174 (7)	C(2)–C(3)	1.402 (9)	P(1)–C(10)	1.846 (8)
Cr–C(4)	2.158 (6)	C(3)–C(4)	1.421 (9)	P(2)–C(11)	1.835 (8)
Cr–C(5)	2.140 (8)	C(4)–C(5)	1.412 (10)	P(2)–C(12)	1.812 (8)
Cr–P(1)	2.450 (2)	C(2)–C(6)	1.527 (11)	P(2)–C(13)	1.818 (8)
Cr–P(2)	2.351 (2)	C(4)–C(7)	1.534 (11)	C(10)–C(11)	1.525 (10)
		Bond Angles (deg)			
P(1)–Cr–Cl	84.36 (6)	C(1)–Cr–C(3)	70.1 (3)	Cr–P(1)–C(8)	119.8 (3)
P(2)–Cr–Cl	92.78 (7)	C(1)–Cr–C(5)	84.7 (3)	Cr–P(1)–C(9)	123.4 (3)
P(1)–Cr–P(2)	81.97 (6)	C(3)–Cr–C(5)	70.3 (3)	Cr–P(1)–C(10)	104.8 (2)
C(1)–C(2)–C(3)	124.3 (7)	C(1)–Cr–P(1)	166.7 (2)	Cr–P(2)–C(11)	110.3 (2)
C(2)–C(3)–C(4)	127.8 (7)	C(1)–Cr–P(2)	85.3 (2)	Cr–P(2)–C(12)	120.4 (3)
C(3)–C(4)–C(5)	122.6 (7)	C(1)–Cr–Cl	100.1 (2)	Cr–P(2)–C(13)	116.0 (3)
C(1)–C(2)–C(6)	118.3 (7)	C(3)–Cr–P(1)	120.6 (2)	C(8)–P(1)–C(9)	101.1 (4)
C(3)–C(2)–C(6)	116.9 (7)	C(3)–Cr–P(2)	150.2 (2)	C(8)–P(1)–C(10)	103.7 (4)
C(3)–C(4)–C(7)	116.5 (7)	C(3)–Cr–Cl	107.6 (2)	C(9)–P(1)–C(10)	101.0 (4)
C(5)–C(4)–C(7)	120.8 (7)	C(5)–Cr–P(1)	91.7 (2)	C(11)–P(2)–C(12)	103.0 (4)
P(1)–C(10)–C(11)	108.4 (5)	C(5)–Cr–P(2)	91.4 (2)	C(11)–C(2)–C(13)	102.7 (4)
P(2)–C(11)–C(10)	109.8 (5)	C(5)–Cr–Cl	173.8 (2)	C(12)–P(2)–C(13)	102.3 (4)

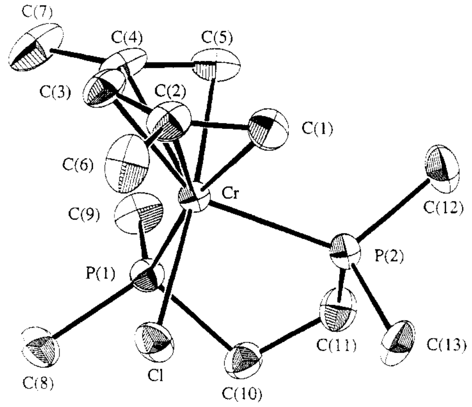
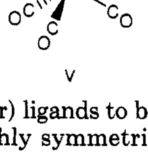


Figure 2. Perspective view and numbering scheme for $Cr(2,4\text{-}C_7H_{11})(Cl)(dmpe)$.

should be more important for the charged C(1,3,5) positions. Thus, it could be expected that π bonding would tend to bring the metal atom toward the open edge of the pentadienyl ligand (by C(1) and C(5)), whereas δ bonding would take the metal atom more toward C(2) and C(4) at the other end. In fact, for $Fe(2,4\text{-}C_7H_{11})_2$, the shortest distances do involve C(2) and C(4), while for $V(2,4\text{-}C_7H_{11})_2$, the shortest bonds are those to C(1) and C(5).

The structural result for $Cr(2,4\text{-}C_7H_{11})(Cl)(dmpe)$ may be seen in Figure 2, and pertinent bonding parameters are presented in Tables IV–VI. Similar to $Fe(2,4\text{-}C_7H_{11})(CO)_2I$[28] and related cyclic dienyl complexes,[29] the coordination geometry about the metal atom can be considered to be approximately octahedral in that the three formally charged carbon atoms are situated opposite the chlorine and two phosphorus atoms, although some distortion of this arrangement can be noted (vide infra). Also noticeable is the fact that the complex has adopted an unsymmetric configuration, with one phosphorus atom lying under the open pentadienyl edge, while the chlorine and other phosphorus atoms reside under the formally uncharged C(2) and C(4) atoms, respectively. Although a related arrangement was found also for $Fe(2,4\text{-}C_7H_{11})(CO)_2I$, the actual arrangement in this case could not be readily deduced without a structural determination due to the paramagnetism of the complex.

The general features of the pentadienyl ligand appear reasonable. The average Cr–C bond distance is 2.161 (3) Å, quite similar to those for $Cr(2,4\text{-}C_7H_{11})_2$ and $Cr(C_5H_5)_2$ (vide supra). The pentadienyl ligand is reasonably planar, although the C(2) and C(4) atoms are bent toward the metal atom by 0.018 and 0.021 Å, while the C(1), C(3), and C(5) atoms are bent the other way by 0.005, 0.027, and 0.007 Å, respectively. As is generally observed, however, the methyl groups are tilted substantially out of the ligand plane (11.4 and 7.7°, respectively) toward the metal atom.[25] Quite possibly, these tilts also bring about the slight deviations of the attached C(2) and C(4) atoms from the ligand planes. The chromium atom lies 1.510 Å from the ligand plane and 1.584 Å from the ligand center of mass. The carbon–carbon bond distances are similar to those for $Cr(2,4\text{-}C_7H_{11})_2$, with the internal, external, and $C\text{–}CH_3$ values averaging 1.411 (7), 1.416 (7), and 1.530 (8) Å, respectively. As is normal, the presence of CH_3 groups on C(2) and C(4) has led to smaller C(1)–C(2)–C(3) and C(3)–C(4)–C(5) angles relative to C(2)–C(3)–C(4), cf. 123.4 (5)° vs 127.8 (7)°.[25] Probably the most notable feature of this structure, however, involves the Cr–P(1) and Cr–P(2) bonds, whose lengths are 2.450 (2) and 2.351 (2) Å, respectively. The large difference in lengths may readily be attributable to the differing electronic requirements of the two sites which are occupied. If one first considers a complex such as $(C_6H_6)Cr(CO)_3$ (V), one would expect all three carbonyl (or other) ligands to bend down to the same extent, leading to highly symmetric (C_{3v}) structures, as have been observed.[30] If one should now replace the arene



V

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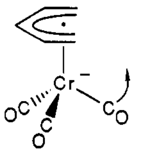
ligand by a pentadienyl anion (or alternatively, add H^- to the arene to generate a cyclohexadienyl anion) yielding VI,



VI

the symmetry has been broken by the formal removal of the sixth metal-bound carbon atom. Without the sixth carbon atom, the metal should have unused orbital density on its right side available for bonding which most likely leads to the upward tilts of the substituents under the pentadienyl edges (e.g., ca. 28° for $Fe(2,4\text{-}C_7H_{11})(CO)_2I$).[28] In the present case, the angles observed between the pentadienyl plane perpendicular and the Cl, P(1), and P(2) atoms are 137.6, 135.2, and 105.5°, respectively, corresponding to an upward tilt by P(2) of 30.9°.[31] As suggested earlier for $Fe(2,4\text{-}C_7H_{11})(CO)_2I$,[28] this difference is likely to lead to a preference of one ligand (thus far not being a σ-bound, one-electron donor such as Cl, I, or CH_3) for this site. As P(2), the upwardly tilted substituent, now is furthest from being opposite to a pentadienyl carbon atom (cf. $\angle C(5)\text{–}Cr\text{–}Cl = 173.8\ (2)°$, $\angle C(1)\text{–}Cr\text{–}P(1) = 166.7\ (2)°$, and $\angle C(3)\text{–}Cr\text{–}P(2) = 150.2\ (2)°$) and presumably has better access to metal orbitals, its bond could well become stronger. Of course, other effects may also be involved (e.g., steric or σ- vs π-bonding considerations), and indeed, in $Fe(2,4\text{-}C_7H_{11})(CO)_2I$, no real difference in the Fe–CO bond distances was observed,[28] while in $Fe(2,4\text{-}C_7H_{11})(PMe_3)_3^+$, a difference of ca. 0.042 (1) Å is present.[29e]

The hydrogen atom positions were refined successfully and yielded an average C–H bond distance of 0.925 (15) Å. As is normal, the endo and exo hydrogen atoms on C(1) and C(5) are bent significantly out of the pentadienyl plane. The bends for the exo hydrogen atoms average 8° toward the chromium atom, while the endo hydrogen atoms average 46° away from the chromium atom. The bonding parameters for the dmpe ligand are reasonable with average $P\text{–}CH_3$, $P\text{–}CH_2$, and C–C distances of 1.823 (4), 1.840 (5), and 1.525 (10) Å, respectively.

Acknowledgment. R.D.E. expresses his gratitude for support of this research from the National Science Foundation and from the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank a reviewer for helpful crystallographic comments.

Registry No. $Cr(2,4\text{-}C_7H_{11})_2$, 80732-73-6; $Cr(dmpe)_3$, 75862-30-5; $Cr(CN(t\text{-}C_4H_9))_6$, 61817-78-5; *trans*-$CrCl_2(dmpe)_2$, 86747-55-9; $Cr(2,4\text{-}C_7H_{11})(Cl)(dmpe)$, 110313-70-7; $K(2,4\text{-}(CH_3)_2C_5H_5)$, 74205-98-4; $Cr(\eta^5\text{-}2,4\text{-}(CH_3)_2C_5H_5)$, 110313-71-8.

Supplementary Material Available: Tables of anisotropic thermal parameters and least-squares plane data for $Cr(2,4\text{-}C_7H_{11})_2$ and $Cr(2,4\text{-}C_7H_{11})(Cl)(dmpe)$ and hydrogen atom parameters for $Cr(2,4\text{-}C_7H_{11})_2$ (5 pages); the structure factor tables (13 pages). Ordering information is given on any current masthead page.

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[31] The respective angles involving the Cr–center of mass vector are more similar, at 127.3, 133.1, and 123.0°, corresponding to a tilt of 7.2°. While this could be taken as an indication that there is actually only little distortion, we suspect the pentadienyl center of mass is not a good criterion for such comparisons. In particular, if one regards a (U) pentadienyl ligand as occupying five of six sites in a hexagon, it is clear that the pentadienyl center of mass is displaced from the equipoint (the center of mass of the hexagon, which would ideally be equidistant from all five or six carbon atoms).

Nonrigidity in $Os_3(CO)_{12-x}[P(OMe)_3]_x$ (x = 1–4)[1]

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The clusters $Os_3(CO)_{12-x}[P(OMe)_3]_x$ (x = 1–4) have been synthesized, from $Os_3(CO)_{12}$ and $P(OMe)_3$ at elevated temperatures, and their stereochemical nonrigidity studied by variable-temperature ^{13}C and ^{31}P NMR spectroscopy. All the clusters exhibit carbonyl exchange in toluene, and, furthermore, isomers are present for $Os_3(CO)_{10}[P(OMe)_3]_2$ and $Os_3(CO)_8[P(OMe)_3]_4$ which are in rapid, nondissociative equilibrium. The changes in the NMR spectra can be completely rationalized in terms of two mechanisms. The first, lower energy process is the well-known, pairwise terminal–bridge carbonyl exchange that involves six carbonyl groups rotating in a plane perpendicular to the Os_3 plane. This exchange appears to not occur in those vertical planes that contain a phosphite ligand: the phosphite is probably prevented from entering an axial site for steric reasons. The second, higher energy process involves the $P(OMe)_3$ ligand of an $Os(CO)_3[P(OMe)_3]$ unit in the cluster moving from one equatorial site to the other via a restricted trigonal-twist mechanism; this simultaneously involves axial–equatorial carbonyl exchange. Once again, it is believed the $P(OMe)_3$ ligand never enters an axial position.

Introduction

In 1982 we reported the preparation of $Ru(CO)_{5-n}[P(OMe)_3]_n$ (n = 1–5) by the ultraviolet irradiation of $Ru_3(CO)_{12}$ and excess $P(OMe)_3$ in hexane.[2] In an extension of this study the corresponding reaction of $Os_3(CO)_{12}$ with $P(OMe)_3$ was investigated. Rather than mononuclear products, the clusters $Os_3(CO)_{12-x}[P(OMe)_3]_x$ (x = 1–6) can be isolated. The clusters with x = 5 and 6 are the most highly substituted derivatives of $Os_3(CO)_{12}$ yet prepared.

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[1] Taken in part from: Alex, R. F. Ph.D. Thesis, Simon Fraser University, 1987.

[2] Alex, R. F.; Pomeroy, R. K. *Organometallics* 1982, *1*, 453.

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