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Symmetric *versus* unsymmetric ligand orientations in (pentadienyl)Cr(I or II)$(L)_2(L')$ species, and a spontaneous reduction of Cr^{II} to Cr^{I}

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Abstract

The reaction of $CrCl_2(PEt_3)_x$ with potassium pentadienide leads to a compound with the stoichiometry of a phosphine adduct of $Cr(C_5H_7)_2$, "$Cr(C_5H_7)_2PEt_3$"; however, dimerization through pentadienyl–pentadienyl coupling actually leads to a Cr^{I} species. Its structure has been determined and suggests little if any contribution from an enediyl Cr^{III} resonance form. The structure of the known $Cr(2,4\text{-}C_7H_{11})(CH_3)(dmpe)$ has also been determined to allow comparison with the former compound.

Compounds of the sort M(pentadienyl)$(L)_2(L')$ have been found to adopt both symmetric and unsymmetric orientations depending upon the nature of L or L′, and on the type of pentadienyl ligand [1–3], bridged species such as cyclohexadienyl displaying differing conformational preferences at times [2]. For the open pentadienyl complexes, electronic effects appear dominant, while both steric and electronic effects are important in the bridged species [2]. To date, most studies have focussed on 18 electron complexes of metals from the manganese and iron groups, and relatively little has been reported either for electron deficient or chromium analogs [4]. Herein we report some observations of the conformational preferences for both 16 and 17 electron chromium complexes.

Experimental

All operations involving organometallics were carried out under a prepurified nitrogen atmosphere in a Schlenk apparatus or in a glovebox. Non-aqueous

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solvents were thoroughly dried and deoxygenated in a manner appropriate to each and were distilled immediately before use [5]. Elemental analyses were performed by Desert Analytics Laboratories. Spectroscopic studies were carried out as previously described [5]. $Cr(2,4-C_7H_{11})(CH_3)(dmpe)$ was prepared as previously described [4] and single crystals were obtained by cooling concentrated solutions in hydrocarbons.

μ-$\eta^4,\eta^{4'}$-*1,3,7,9-Decatetraenebis[(triethylphosphine)(pentadienyl)chromium(I)].* $[Cr(C_5H_7)P(C_2H_5)_3]_2(\mu\text{-}\eta^4,\eta^{4'}\text{-}1,3,7,9\text{-}C_{10}H_{14})$

A mixture of $CrCl_3 \cdot 3THF$ [6] (1.00 g, 2.68 mmol) and zinc dust (approx. 0.05 g) in 20 mL of THF was stirred for 1 h or until no sign of purple $CrCl_3 \cdot 3THF$ remained. At this point, triethylphosphine (0.85 mL, 5.75 mmol) was added to the slurry of "$CrCl_2$" and stirred for 5–10 min, resulting in a deep blue solution of $CrCl_2 \cdot nPEt_3$. After cooling this solution to -78°C, $K(C_5H_7)$ [7] (0.60 g, 5.65 mmol) in 40 mL of THF was added dropwise over 15 min. The reaction mixture was allowed to warm slowly, then stirred for at least 2 h at ambient temperature before the solvent was removed *in vacuo* and the remaining residues extracted with three 15-mL portions of hot hexanes and filtered through Celite. Crystals suitable for X-ray diffraction (m.p. 132–135°C, dec.) were obtained by slowly cooling the hexane solution to approx. 0°C. Further cooling of the concentrated supernatant to -20°C afforded 0.50 g (78% yield) of the green product in a powdered form. Anal. Found: C, 62.84; H, 9.38. $C_{32}H_{58}Cr_2P_2$ calc.: C, 63.14; H, 9.60%.

Infrared data (Nujol mull): 1420m, 1257m, 1213m, 1175w, 1089m, 1045sh, 1031s, 978mw, 950vw, 929m, 851m, 827mw, 800w, 758s, 737m, 727m, 700m, 692sh, 672w, 645w, 610vw cm^{-1}. Mass spectrum: m/e (relative intensity): 41(37), 61(46), 62(78), 67(100), 90(63), 118(41), 186(0.32) (highest detectable m/e due to $Cr(C_5H_7)_2$). EPR (toluene, amb.): $g = 1.996$; $A = 15.8$ G.

Single crystal X-ray diffraction studies

For $[Cr(C_5H_7)P(C_2H_5)_3]_2(C_{10}H_{14})$, the pertinent data collection and refinement parameters are provided in Table 1. The initial space group choice of $P\bar{1}$ was indicated to be correct by the successful solution and refinement of the structure, and an empirical correction for absorption was applied (range, 0.919–1.000). The structure was solved using direct methods, which revealed the locations of the independent chromium atoms. The remaining non-hydrogen atoms were then located from difference Fourier maps, and generally subjected to anisotropic refinement. However, several of the phosphine carbon atoms were rather poorly behaved, presumably due to positional disorder and high thermal motion, and had to be treated isotropically. C(21) proved to be particularly troublesome, and its bonding parameters must be considered suspect. Such disorder problems are not uncommon for PEt_3 ligands [8]. Hydrogen atoms were placed in calculated positions and given isotropic thermal parameters ($B = 5$ Å^2). Pertinent positional and bonding parameters are given in Tables 2 and 3. Additional structural information may be obtained from the authors.

For $Cr(2,4-C_7H_{11})(CH_3)(dmpe)$, the crystal, data collection and refinement parameters are also collected in Table 1. A dark brown crystal, suitable for X-ray diffraction study, was mounted on a fine glass fiber with epoxy cement. The unit

Table 1

Crystallographic data

(a) *Crystal parameters*		
Formula	$C_{32}H_{58}P_2Cr_2$	$C_{14}H_{26}P_2Cr$
Formula weight	608.76	308.30
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$
a (Å)	10.617(2)	9.456(5)
b (Å)	12.512(3)	14.506(6)
c (Å)	13.237(3)	12.657(4)
α	101.84(2)	90
β	77.64(2)	90
γ	107.95(2)	90
V (Å^3)	1615.6	1736.1(12)
Z	2	4
Crystal dimensions (mm^3)	0.30×0.23×0.13	0.26×0.32×0.36
Crystal color	Green	Dark brown
D(calc.) (g cm^{-3})	1.251	1.179
μ (Mo-K$_\alpha$) (cm^{-1})	7.72	8.07
Temperature (K)	289	297
T(max)/T(min)	1.088	1.055
(b) *Data collection*		
Diffractometer	Nicolet $P\bar{1}$	Nicolet $R3m$
Monochromator	Graphite	Graphite
Radiation	Mo-K_α(λ = 0.71073 Å)	Mo-K_α(λ = 0.71073 Å)
2θ scan range (deg)	2.5–43.0	4–50
Data collected (h, k, l)	+13, ±15, ±16	+12, +18, +16
Independent reflections	3477	1756
Independent observed reflections $F_o \geq n\sigma(F_o)$	2564 (n = 3)	1414 (n = 5)
Standard reflections	2 standard/100 reflections	3 standard/197 reflections
Variation in standards	< 2	< 2
(c) *Refinement*		
$R(F)$ (%)	6.54	4.81
$R(wF)$ (%)	7.02	5.05
Δ/σ(max)	0.04	0.032
$\Delta(\rho)$, (e Å^{-3})	0.56	0.387
N_o/N_v	8.4	9.2
GOF	2.54	1.328

cell parameters were obtained from the least squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). Preliminary photographic characterization showed *mmm* Laue symmetry and the systematic absences in the diffraction data uniquely established the space group as $P2_12_12_1$. The usual tests for handedness were performed but the results were statistically insignificant. No absorption correction was applied to the data (low μ, $T_{max}/T_{min} = 1.055$). The structure was solved by direct methods which located the Cr atom. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses. The hydrogen atoms were included as idealized isotropic contributions (d(CH) = 0.960 Å, U = 1.2 U for attached C). All non-hydrogen atoms were refined with anisotropic thermal parameters. Table 4

Table 2

Atomic coordinates ($\times 10^4$) for $Cr_2P_2C_{32}H_{58}$

	x	*y*	*z*
Cr(1)	0.4393(1)	0.3382(1)	0.7288(1)
Cr(2)	−0.1074(1)	0.2474(1)	1.2443(1)
P(1)	0.5738(3)	0.2596(2)	0.7984(2)
P(2)	0.0383(2)	0.1804(2)	1.3147(2)
C(1)	0.525(1)	0.4928(8)	0.8309(8)
C(2)	0.435(1)	0.5126(8)	0.7753(8)
C(3)	0.436(1)	0.4847(8)	0.6672(8)
C(4)	0.519(1)	0.4255(9)	0.5940(7)
C(5)	0.625(1)	0.3932(9)	0.6185(8)
C(6)	−0.163(1)	0.0786(8)	1.1509(8)
C(7)	−0.2372(9)	0.1457(9)	1.1325(8)
C(8)	−0.3088(9)	0.209(1)	1.2100(9)
C(9)	−0.3108(9)	0.2246(9)	1.3198(8)
C(10)	−0.2537(9)	0.1679(8)	1.3703(8)
C(11)	0.360(1)	0.1662(9)	0.6452(8)
C(12)	0.272(1)	0.243(1)	0.6592(8)
C(13)	0.2235(9)	0.282(1)	0.7603(8)
C(14)	0.2649(9)	0.2675(8)	0.8480(7)
C(15)	0.224(1)	0.3328(8)	0.9543(8)
C(16)	0.1061(9)	0.2599(8)	1.0203(7)
C(17)	0.0683(9)	0.3213(8)	1.1273(7)
C(18)	−0.0330(9)	0.3790(8)	1.1474(7)
C(19)	−0.0767(9)	0.4238(8)	1.2508(8)
C(20)	−0.024(1)	0.4134(8)	1.3348(7)
C(21)	0.530(2)	0.263(2)	0.953(2)
C(22)	0.460(2)	0.173(1)	0.992(1)
C(23)	0.740(1)	0.351(1)	0.814(1)
C(24)	0.835(1)	0.308(1)	0.854(1)
C(25)	0.574(2)	0.112(2)	0.762(1)
C(26)	0.631(1)	0.082(1)	0.641(1)
C(27)	0.2199(9)	0.2525(8)	1.2877(8)
C(28)	0.315(1)	0.212(1)	1.3336(9)
C(29)	0.012(1)	0.1840(9)	1.4587(8)
C(30)	0.027(1)	0.299(1)	1.5249(9)
C(31)	0.036(1)	0.0286(8)	1.2787(9)
C(32)	0.110(1)	−0.001(1)	1.167(1)

contains positional parameters and Table 5 contains relevant bond distances and bond angles. Additional bonding parameters may be obtained from the authors.

All computer programs and the sources of the scattering factors are contained in the SHELXTL program library (5.1) (G. Sheldrick, Nicolet (Siemens), Madison, WI).

Results and discussion

The reaction of $CrCl_2(PEt_3)_n$ with two equivalents of KC_5H_7 leads to the formation of a complex of stoichiometry $Cr(C_5H_7)_2PEt_3$:

$$CrCl_2(PEt_3)_n + 2KC_5H_7 \rightarrow \text{“}[Cr(C_5H_7)_2(PEt_3)]_2\text{”} \qquad (1)$$

Table 3

Bond distances and bond angles for $Cr_2P_2C_{32}H_{58}$

Bond distances (Å)			
Cr(1)-P(1)	2.379(2)	Cr(2)-P(2)	2.387(2)
Cr(1)-C(1)	2.182(7)	Cr(2)-C(6)	2.193(7)
Cr(1)-C(2)	2.153(7)	Cr(2)-C(7)	2.175(7)
Cr(1)-C(3)	2.165(7)	Cr(2)-C(8)	2.169(7)
Cr(1)-C(4)	2.162(7)	Cr(2)-C(9)	2.135(7)
Cr(1)-C(5)	2.201(7)	Cr(2)-C(10)	2.192(7)
Cr(1)-C(11)	2.206(8)	Cr(2)-C(17)	2.241(6)
Cr(1)-C(12)	2.122(7)	Cr(2)-C(18)	2.148(7)
Cr(1)-C(13)	2.153(6)	Cr(2)-C(19)	2.116(7)
Cr(1)-C(14)	2.239(7)	Cr(2)-C(20)	2.198(7)
P(1)-C(21)	2.00(2)	P(2)-C(27)	1.85(1)
P(1)-C(23)	1.81(1)	P(2)-C(29)	1.86(2)
P(1)-C(25)	1.81(2)	P(2)-C(31)	1.86(2)
C(21)-C(22)	1.28(2)	C(27)-C(28)	1.53(2)
C(23)-C(24)	1.51(1)	C(29)-C(30)	1.51(3)
C(25)-C(26)	1.59(1)	C(31)-C(32)	1.55(2)
C(1)-C(2)	1.42(1)	C(6)-C(7)	1.40(1)
C(2)-C(3)	1.40(1)	C(7)-C(8)	1.40(1)
C(3)-C(4)	1.42(1)	C(8)-C(9)	1.42(1)
C(4)-C(5)	1.43(1)	C(9)-C(10)	1.40(1)
C(11)-C(12)	1.41(1)	C(19)-C(20)	1.39(1)
C(12)-C(13)	1.41(1)	C(18)-C(19)	1.406(9)
C(13)-C(14)	1.39(1)	C(17)-C(18)	1.423(9)
C(14)-C(15)	1.525(9)	C(16)-C(17)	1.503(9)
C(15)-C(16)	1.521(9)		
Bond angles (deg)			
Cr(1)-P(1)-C(21)	114.4(4)	Cr(2)-P(2)-C(27)	116.9(3)
Cr(1)-P(1)-C(23)	115.5(3)	Cr(2)-P(2)-C(29)	118.4(5)
Cr(1)-P(1)-C(25)	112.0(1)	Cr(2)-P(2)-C(31)	118.8(4)
P(1)-C(21)-C(22)	120(1)	P(2)-C(27)-C(28)	117.6(7)
P(1)-C(23)-C(24)	119.8(8)	P(2)-C(29)-C(30)	117(1)
P(1)-C(25)-C(26)	112.8(5)	P(2)-C(31)-C(32)	114(1)
C(21)-P(1)-C(23)	89.1(6)	C(27)-P(2)-C(29)	101.1(4)
C(21)-P(1)-C(25)	98.1(5)	C(27)-P(2)-C(31)	101.7(4)
C(23)-P(1)-C(25)	111.4(4)	C(29)-P(2)-C(31)	96.3(8)
C(1)-C(2)-C(3)	125.8(7)	C(6)-C(7)-C(8)	125.3(7)
C(2)-C(3)-C(4)	126.9(7)	C(7)-C(8)-C(9)	126.7(7)
C(3)-C(4)-C(5)	124.4(7)	C(8)-C(9)-C(10)	125.4(7)
C(11)-C(12)-C(13)	120.4(7)	C(18)-C(19)-C(20)	122.0(6)
C(12)-C(13)-C(14)	121.2(7)	C(17)-C(18)-C(19)	119.4(6)
C(13)-C(14)-C(15)	119.4(6)	C(16)-C(17)-C(18)	121.1(6)
C(14)-C(15)-C(16)	112.3(6)	C(15)-C(16)-C(17)	113.0(6)

Although such a species could possess an 18-electron configuration (*cf.* $Cr(C_5H_5)_2CO$), this compound is dimeric, unlike its titanium and vanadium analogs. The compound is paramagnetic (1 unpaired electron/Cr), and exhibits a well defined ESR signal in the $g = 2$ region (Fig. 1). Notably, a strong ESR signal (singlet, $g = 1.995$) has also been observed [9] for the purportedly diamagnetic "$[Cr(C_5H_7)_2(CO)]_2$" [10], which suggests a structural relationship between the two.

Table 4

Atomic coordinates and isotropic thermal parameters (Å^2) for $CrP_2C_{14}H_{26}$

	x	y	z	U [a]
Cr	1.1256(1)	0.15557(6)	0.26583(8)	0.0357(5)
P(1)	1.0382(2)	0.1015(1)	0.4332(2)	0.050(1)
P(2)	0.8918(2)	0.1363(1)	0.2162(2)	0.057(1)
C(1)	1.1630(9)	0.1933(6)	0.1034(6)	0.070(3)
C(2)	1.2868(9)	0.2094(6)	0.1603(7)	0.064(3)
C(3)	1.3509(8)	0.1462(5)	0.2292(7)	0.064(3)
C(4)	1.3008(8)	0.0570(6)	0.2581(7)	0.061(3)
C(5)	1.1813(9)	0.0154(5)	0.2144(7)	0.070(3)
C(6)	1.3486(10)	0.3069(6)	0.1611(9)	0.095(4)
C(7)	1.3791(9)	0.0097(7)	0.3468(9)	0.099(4)
C(8)	0.8520(9)	0.1265(7)	0.4320(8)	0.093(4)
C(9)	0.7864(9)	0.0943(8)	0.3296(9)	0.106(5)
C(10)	1.0992(14)	0.1535(7)	0.5547(6)	0.105(5)
C(11)	1.0385(9)	−0.0201(6)	0.4681(7)	0.068(8)
C(12)	0.7911(9)	0.2392(6)	0.1751(8)	0.077(3)
C(13)	0.8418(12)	0.0559(7)	0.1138(9)	0.116(5)
C(14)	1.0839(7)	0.2929(4)	0.3314(5)	0.038(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 5

Bond distances and bond angles for $C_{14}H_{26}P_2Cr$

Bond distances (Å)			
Cr–P(1)	2.405(2)	Cr–P(2)	2.315(2)
Cr–C(1)	2.157(8)	Cr–C(2)	2.173(9)
Cr–C(3)	2.185(7)	Cr–C(4)	2.191(8)
Cr–C(5)	2.199(8)	Cr–C(14)	2.193(6)
C(1)–C(2)	1.394(12)	C(2)–C(3)	1.403(12)
C(2)–C(6)	1.529(13)	C(3)–C(4)	1.426(11)
C(4)–C(5)	1.395(11)	C(4)–C(7)	1.509(13)
Bond angles (deg)			
P(1)–Cr–P(2)	82.6(1)	P(1)–Cr–C(1)	168.1(2)
P(1)–Cr–C(14)	84.3(2)	P(1)–Cr–C(3)	120.1(2)
P(2)–Cr–C(14)	92.3(2)	P(1)–Cr–C(5)	92.4(2)
C(14)–Cr–C(1)	99.2(3)	P(2)–Cr–C(1)	85.9(2)
C(14)–Cr–C(3)	108.2(3)	P(2)–Cr–C(3)	150.0(2)
C(14)–Cr–C(5)	174.1(3)	P(2)–Cr–C(5)	92.1(2)
C(1)–C(2)–C(3)	125.0(8)	C(1)–C(2)–C(6)	118.7(8)
C(3)–C(2)–C(6)	115.7(8)	C(2)–C(3)–C(4)	127.5(7)
C(3)–C(4)–C(5)	124.0(7)	C(3)–C(4)–C(7)	116.1(7)
C(5)–C(4)–C(7)	119.7(7)	Cr–P(1)–C(8)	105.3(3)
Cr–P(1)–C(10)	120.2(4)	Cr–P(1)–C(11)	122.0(3)
Cr–P(2)–C(9)	110.1(3)	Cr–P(2)–C(12)	118.1(3)
Cr–P(2)–C(13)	121.5(4)	P(1)–C(8)–C(9)	110.3(7)
P(2)–C(9)–C(8)	110.1(7)		

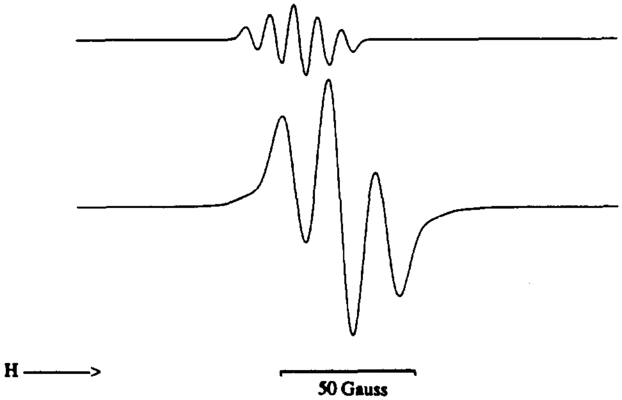


Fig. 1. ESR spectrum of the $[Cr(C_5H_7)P(C_2H_5)_3]_2(\mu\text{-}\eta^4,\eta^{4'}\text{-}1,3,7,9\text{-}C_{10}H_{14})$ dimer. Shown above is the signal for DPPH.

To establish the structures of these compounds, a single crystal diffraction study was carried out on the PEt_3 adduct (Fig. 2, Tables 1, 2). The structural result reveals that an intermolecular coupling of pentadienyl ligands has taken place,

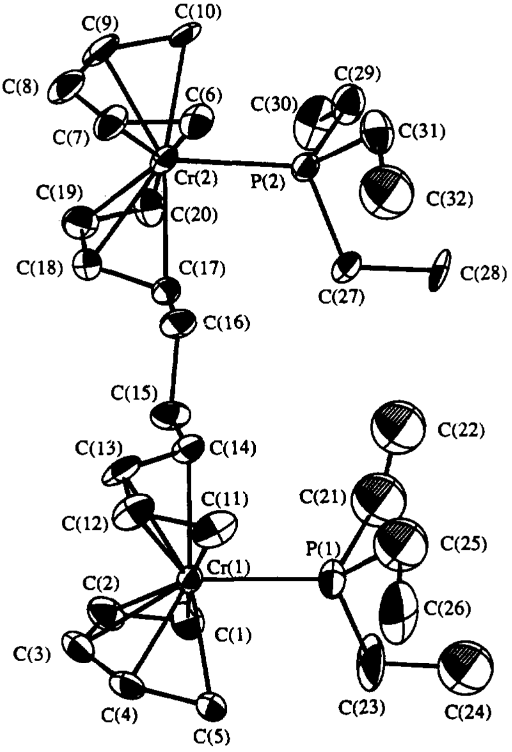
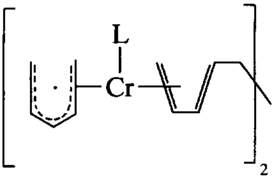


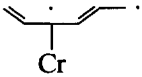
Fig. 2. Perspective view and numbering scheme for the $[Cr(C_5H_7)P(C_2H_5)_3]_2(\mu\text{-}\eta^4,\eta^{4'}\text{-}1,3,7,9\text{-}C_{10}H_{14})$ dimer.

resulting in the Cr^I complex **I** ($L = PEt_3$). While related intermolecular couplings

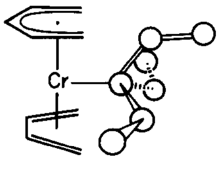


(I)

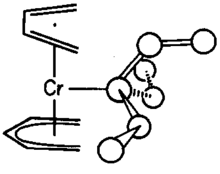
have been observed [11], in general they occur in cases in which formal 19-electron complexes have been generated, which then regain the 18-electron configuration through dimerization. The present coupling reaction is unusual in that the electron count drops from 18 to 17 electrons, while Cr^{II} is spontaneously reduced to Cr^I. As neither conversion is at all common, this seems to provide another indication of the tendency for metal pentadienyl compounds to favor low oxidation states. It seems quite possible also that steric crowding could contribute to the coupling, as the probable intermediate, $Cr(2,4\text{-}C_7H_{11})_2(PEt_3)$, would be expected to possess one η^5-U and one η^5-S (S = sickle) pentadienyl ligand, as observed for its molybdenum and tungsten analogs [1,12], as well as in $Cr(C_5H_5)(Pdl)(L)$ complexes (Pdl = C_5H_7, 3-C_6H_9, 2,4-C_7H_{11}, *etc.*; L = CO, PF_3, PR_3, $P(OR)_3$, RNC) [13]. However, for a smaller atom such as chromium, the tilt of the handle end of the sickle toward the metal center would be expected to generate severe steric problems, since the dienyl ligand planes are already within a van der Waals separation. The handle may then be unable to achieve a favorable interaction with the chromium atom, leading to an increased contribution of the type below, and to the observed dimerization [14*]. Although Cr^I complexes are relatively uncommon, it can be noted that a number of 17-electron cyclopentadienyl analogs are also known, particularly species derived from the formal replacement of CO ligands in $[Cr(C_5H_5)(CO)_3]_2$ by bulkier ligands such as $P(C_6H_5)_3$, which then render the complex sufficiently crowded that Cr–Cr bond formation is unfavorable [15].



The dienyl-diene orientations are similar to that observed in a Ru(η^5-dienyl)(η^4-diene)(CO)$^+$ structure [2], although the two independent chromium centers differ slightly by virtue of the placement of the phosphine ethyl groups (**IIa**,**b**). While both phosphines have one arm bent back and two to the sides, as is



(IIa)



(IIb)

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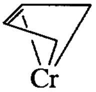
* Reference number with asterisk indicates a note in the list of references.

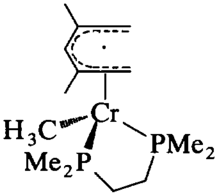
commonly observed in these relatively crowded molecules [16], for Cr(1) the unique arm is located near the open diene edge, while for Cr(2) the unique arm resides near the open dienyl edge. This therefore minimizes interphosphine ethyl–ethyl repulsions, and could be responsible for the complexity of the compound's ESR spectrum [17*]

The Cr–dienyl bonding patterns for the two fragments are similar, with average Cr–C(1, 5), Cr–C(2, 4), and Cr–C(3) bond distances of 2.192(10), 2.156(10), and 2.167(5) Å, respectively. For comparison, the average Cr–C bond distance in $Cr(2,4-C_7H_{11})_2$ [4] is 2.163(3) Å. The C–C–C bond angles around the C(2, 4) and C(3) positions are similar, averaging 125.2(4)° and 126.8(5)°, respectively. The bonding patterns in the two Cr–diene fragments are also similar, although the presence of a substituent on one end of each diene does destroy the mirror symmetry that might have been expected. However, the Cr–C (internal) bonds can be seen to be shorter than their respective Cr–C (external) bonds, the values for the less crowded side averaging 2.119(5) *versus* 2.202(5) Å, compared to 2.151(5) versus 2.240(5) Å for the more crowded (substituted) end. Together with the fact that the dienes' internal and external C–C bond lengths are all fairly similar, these data do not seem to provide any support for the formulation of this compound as a Cr^{III}-enediyl species (**III**). The Cr–P bond lengths average 2.383(2) Å, similar to the values found in $Cr(2,4-C_7H_{11})(X)(dmpe)$ structures ($X = Cl$ [4] or CH_3, *vide infra*).



(III)

The structure of the related 16-electron Cr^{II} complex, $Cr(2,4-C_7H_{11})(CH_3)$-(dmpe), was also of interest. This compound was expected to adopt an unsymmetric configuration, analogous to $Cr(2,4-C_7H_{11})(Cl)(dmpe)$ [4], in which the site under the open dienyl edge was occupied by one phosphorus atom, while the second occupied a site under a formally uncharged dienyl carbon atom, as in **IV**. However, the paramagnetic nature of the compound precluded NMR spectral confirmation. A diffraction study has now confirmed the unsymmetric structure (Fig. 3), in which the methyl group resides under one of the formally uncharged dienyl carbon atoms. The two Cr–P bonds are therefore non-equivalent and have lengths of 2.405(2) Å (P(1)) and 2.315(2) Å (P(2)). As in the various other $M(dienyl)(L)_3$ or $M(dienyl)(L)(L')_2$ structures [2,4,18], it is the ligand under the open dienyl edge which experiences a favored interaction, which may be traced to the presence of unused metal orbital density in that location. Earlier structures



(IV)

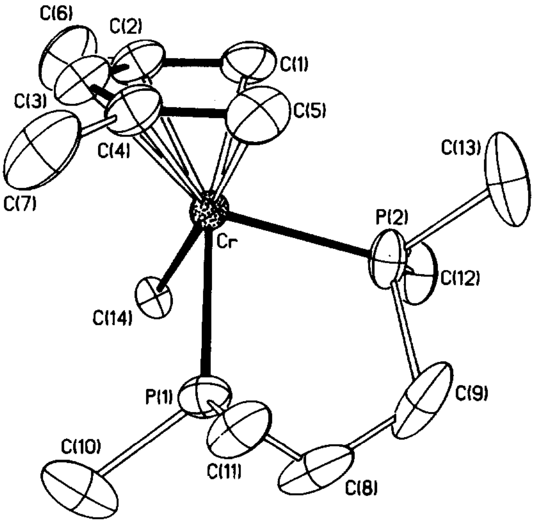


Fig. 3. Perspective view and numbering scheme for $Cr(2,4-C_7H_{11})(CH_3)(dmpe)$.

had revealed that the relative tendencies for ligands to occupy this site fell in the order $R_3P > CO$ [2] and $CO > I$, CH_3 [18], from which one would expect a preference of $R_3P > CH_3$, as observed. A second consequence of the presence of the unused metal orbital density is the fact that the ligand in the unique site experiences an upward tilt toward the pentadienyl plane. In this case, P(2) is found to be 2.148 Å below this plane, compared to 3.273 Å for P(1) (C(14), 3.125 Å; Cr, 1.533 Å). The methyl groups are found under the pentadienyl plane (0.232, 0.206 Å), corresponding to respective tilts of 8.7° and 7.8°.

For the most part, the Cr–dienyl bonding appears reasonable, with average Cr–C(1, 5), Cr–C(2, 4), and Cr–C(3) distances of 2.178(6), 2.182(6), and 2.185(7) Å, respectively. However, the Cr–C(5) bond does appear to be longer than the Cr–C(1) bond, 2.199(8) *versus* 2.157(8) Å, which seems to be at odds with the relative *trans* influences of phosphine and alkyl ligands and may point to a steric interaction between C(5) and the dmpe ligand [19]. The $Cr-CH_3$ bond length of 2.193(6) Å is actually not clearly different from the Cr–C(dienyl) bond lengths. For comparison, in both $Fe(2,4-C_7H_{11})(I)(CO)_2$ [18] and $Fe(cycloheptadienyl)(CH_3)(CO)[P(OC_6H_5)_3]$ [20], the Fe–dienyl and $Fe-CH_3$ distances were found to be *ca.* 2.133 and 2.113 Å, respectively – also quite similar. The $Cr-CH_3$ distance is 0.161(6) Å shorter than the Cr–Cl distance of 2.354(2) Å in $Cr(2,4-C_7H_{11})(Cl)(dmpe)$, consistent with the differences in sizes of carbon and chlorine atoms, if some shortening of the Cr–Cl bond is allowed for as a result of the significant difference in their electronegativities [21].

In the related complex, $Cr(C_5Me_5)(CH_3)(dmpe)$, the average $Cr-C(C_5Me_5)$ and Cr–alkyl bond distances were found to be 2.243 and 2.150(10) Å, respectively, while for various Cr^{III} analogs, even greater differences were observed [22]. As in the case of $M(C_5H_5)(Pdl)(PEt_3)$ (M = Ti [23]; Pdl = $2,4-C_7H_{11}$; M = V [24], Pdl = C_5H_7) or $Cr(C_5Me_5)(C_5H_7)$ [13], one observes a significant shortening for the open pentadienyl ligand relative to the closed system, which seems to reflect a stronger bonding interaction between metal and pentadienyl for at least the early transition metals. The bonding parameters within the dienyl ligand are reasonable, with C–C (internal), C–C (external), and C–CH_3 distances averaging 1.395(8), 1.415(8), and 1.519(9) Å, respectively. The presence of methyl groups on C(2) and C(4) leads to the usual contraction of the respective C(1)–C(2)–C(3) and C(3)–C(4)–C(5) angles relative to C(2)–C(3)–C(4) (125.0(8)°, 124.0(7)°, and 127.5(7)°), and the methyl groups are located an average of 0.219 Å below the pentadienyl ligand plane, corresponding to an average tilt of 8.3°.

The results above demonstrate that the same factors which control ligand orientations in 18 electron M(dienyl)(L)$_2$(L′) complexes are also operative in 16 and 17 electron species. Furthermore, the spontaneous conversion of a Cr^{II} to a Cr^{I} complex is particularly unusual and would seem to reflect the steric crowding and favorability of low oxidation states which generally characterize metal pentadienyl compounds. While open titanocenes and vanadocenes readily form a variety of mono(ligand) adducts, the analogous complexes of the smaller chromium atom appear too crowded to be reasonably stable, an effect which must be exacerbated by the desire of one of the pentadienyl ligands to adopt the unusual η^5-sickle mode of coordination in such adducts.

Acknowledgments

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