Chemical Synthesis with Metal Atoms. The Preparation and Structure of Cyclo-octadiene Trifluorophosphine Complexes of Chromium. The Crystal Structure of (η^5-Cyclo-octa-1,3-dienyl)hydridotris(trifluorophosphine)chromium

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The reaction of cyclo-octa-1,5-diene (1,5-cod), PF_3, and chromium atoms produces $[Cr(1,5\text{-cod})(PF_3)_4]$ (1) and $[Cr(C_8H_{11})(PF_3)_3H]$ (2). The use of 1,3- rather than 1,5-cod produces only (2) under the same conditions. Complex (1) is readily converted into (2) by heating (90 °C, in toluene). The preparation of $[Cr(1,5\text{-cod})(CO)_4]$ (3) from 1,3- or 1,5-cod is also described. The structure of (2) was determined by *X*-ray crystallography. The compound crystallizes in the orthorhombic space group *Pbca* with $a = 13.452(3)$, $b = 14.419(4)$, $c = 15.268(3)$ Å, and $Z = 8$. The final *R* value was 0.065 9 for 1 699 observed reflections. The structure is retained in solution below −80 °C, but is shown by ^{13}C and ^1H n.m.r. spectroscopy to become fluxional upon warming. There are two distinct exchange processes; one results in pairwise coalescence of the ^{13}C and ^1H resonances; the other finally leads to a set of only two ^1H signals with an intensity ratio of 8 : 4, thus indicating equivalence of the eight ring positions.

THE reaction of chromium atoms with unsaturated hydrocarbons is well known.[1] The reaction procedure involves the co-deposition of metal atoms and hydrocarbon at low temperatures (−196 °C) usually on an inert matrix at pressures of between 10^{-3} and 10^{-5} Torr.[2,†]

The preparation of arene sandwich compounds from substituted benzenes and chromium atoms has been standardized.[3] Organochromium complexes which do not conform to the 18-electron rule can often be stabilized by the subsequent addition of CO or PF_3, although electron configurations other than those of a closed shell are sometimes associated with stable compounds. Thus, the reaction of chromium atoms with cycloheptatriene leads initially to $[Cr(C_7H_8)_2]$,[4] an 18-electron complex which subsequently rearranges to $[Cr(C_7H_7)(C_7H_{10})]$, formally a 17-electron complex, on warming to room temperature;[5] introduction of PF_3 at −196 °C after the co-deposition process leads to the isolation of $[Cr(C_7H_8)(PF_3)_3]$, the expected 18-electron complex.

Cyclo-octa-1,5-diene (1,5-cod) forms a variety of well defined transition-metal complexes, the stability of which has been ascribed to the chelating character of this ligand.[6] In contrast, isolated complexes of 1,3-cod are quite rare.[7,8] Chromium(0) complexes of 1,3-cod are unknown,[9] whereas with 1,5-cod a tetracarbonylchromium complex has been reported in 2% yield from the thermal reaction of $[Cr(CO)_6]$ with 1,5-cod. Attempts to replace CO in $[Cr(1,5\text{-cod})(CO)_4]$ by cyclo-octadiene have been unsuccessful because of the ease of elimination of 1,5-cod.[10]

We have therefore investigated the co-condensation of 1,3- and 1,5-cod with chromium atoms, with subsequent exposure to CO, as an alternative synthetic route.

RESULTS AND DISCUSSION

The co-deposition of chromium atoms with 1,3- or 1,5-cod at −196 °C on a pentane matrix and subsequent addition of CO led to the formation of tetracarbonyl(η^4-cyclo-octa-1,5-diene)chromium, $[Cr(1,5\text{-cod})(CO)_4]$ (3); cyclo-octa-1,3-diene complexes could not be isolated. Complex (3) showed four i.r.-active CO vibrations consistent with the expected C_{2v} symmetry. A corresponding isomerization of a 1,3- to a 1,5-diene configuration has been observed in the thermal reaction of 1,3-cod with $[Mo(CO)_6]$ and $[W(CO)_6]$ leading to the 1,5-cod complexes.[11]

Similar reactions using PF_3 rather than CO as a stabilizing ligand are more complicated. Reaction of 1,3-cod, chromium atoms, and PF_3 led only to (1—5-η-cyclo-octa-1,3-dienyl)hydridotris(trifluorophosphine)-chromium, $[Cr(C_8H_{11})(PF_3)_3H]$ (2). Reaction of 1,5-cod, chromium atoms, and PF_3 yielded a separable mixture of (η^4-cyclo-octa-1,5-diene)tetrakis(trifluorophosphine)-chromium (1) and $[Cr(C_8H_{11})(PF_3)_3H]$ (2). Complex (1) can be converted into (2) by warming a solution of it to 90 °C. The ^1H n.m.r. spectra of (1) and (3) are almost identical, and the ^{19}F n.m.r. spectrum of (1) showed two equally intense non-equivalent doublets consistent with the expected C_{2v} symmetry. Yields and reaction conditions are summarized in Scheme 1.

Characterization of Complex (2).—X-*Ray structure*. The *X*-ray structure of (2) was deduced from 2 916 diffractometer-collected reflections (*hkl*, *h̄kl*) from a crystal of dimensions 0.35 × 0.68 × 0.19 mm. The collected reflections were averaged to 1 699 (*hkl*) unique reflections (280 unobserved) for which $I/\sigma(I) \leqslant 2.0$. Using the heavy-atom method, a final *R* value of 0.065 9 (*R'* 0.086 8) was obtained. For details of data collection and computing procedures see ref. 12. Scattering factors used were those of Cromer and Waber [13] for the

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† Throughout this paper: 1 Torr = (101 325/760) Pa.

heavier atoms and of Stewart *et al.*[14] for hydrogen atoms.

Crystal data. $C_8H_{12}CrF_9P_3$, $M = 424.11$, $a = 13.452(3)$, $b = 14.419(4)$, $c = 15.268(3)$ Å, $U = 2\,961.42$ Å^3, $Z = 8$, $D_c = 1.902$ g cm^{-3}, space group *Pbca*, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 12.21$ cm^{-1}.

The structure analysis was seriously hampered by rotational disorder of the PF_3 groups. Partial-occupancy factors were assigned to all the fluorine atoms in the final stage of the anisotropic least-squares refinement. Best hydrogen-atom positions were computed and these were compared with a difference-Fourier synthesis which did not reveal all these calculated positions. Hydrogen-atom parameters were therefore not varied in the final cycles of the refinement. Final atomic co-ordinates are given in Table 1; a selection of significant bond lengths and angles is in Table 2. Structure factor tables and thermal parameters are given in Supplementary Publication No. SUP 22957 (9 pp.).*

TABLE 1

Final atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cr	1 398(1)	1 391(1)	1 344(1)
P(1)	1 245(2)	2 084(2)	2 567(1)
P(2)	582(2)	214(1)	1 823(1)
P(3)	97(1)	2 133(2)	897(2)
F(1)	1 513(8)	3 089(6)	2 732(6)
F(2)	230(5)	2 287(6)	3 001(4)
F(3)	1 837(7)	1 780(8)	3 421(5)
F(4)	−569(5)	176(6)	1 831(5)
F(5)	646(7)	−744(6)	1 306(6)
F(6)	794(9)	−222(8)	2 712(8)
F(7)	59(7)	3 206(6)	882(8)
F(8)	−911(5)	2 067(8)	1 295(7)
F(9)	−229(9)	2 026(12)	−65(8)
C(1)	2 785(6)	2 057(6)	1 063(6)
C(2)	2 257(6)	2 014(6)	286(5)
C(3)	1 871(8)	1 196(8)	−127(6)
C(4)	2 718(9)	545(11)	−541(7)
C(5)	3 479(8)	202(8)	78(7)
C(6)	3 060(9)	−244(8)	891(9)
C(7)	2 693(6)	418(9)	1 648(7)
C(8)	2 943(7)	1 338(8)	1 686(7)
F(1B) *	1 867(16)	3 105(13)	2 618(13)
F(3B) *	1 510(13)	1 571(12)	3 422(11)
F(45) *	−325(21)	−148(21)	1 355(17)
F(46) *	242(19)	163(19)	2 782(16)
F(56) *	995(14)	−740(14)	1 870(13)
F(78) *	−576(19)	2 535(20)	1 543(17)
F(79) *	53(18)	2 853(20)	300(17)
F(89) *	−733(22)	1 617(20)	625(19)
H(001)	3 090	2 685	1 226
H(002)	2 133	2 614	−9
H(003)	1 399	1 388	−619
H(004)	1 474	815	300
H(005)	3 049	884	−1 033
H(006)	2 376	−30	−816
H(007)	3 890	740	285
H(008)	3 942	−253	−225
H(009)	3 571	−698	1 131
H(010)	2 472	−657	680
H(011)	2 228	205	2 079
H(012)	3 328	1 513	2 219

* F(1B) and F(3B) are partial positions close to F(1) and F(3) respectively; the other F(*mn*) positions are partial atoms located between F(*m*) and F(*n*).

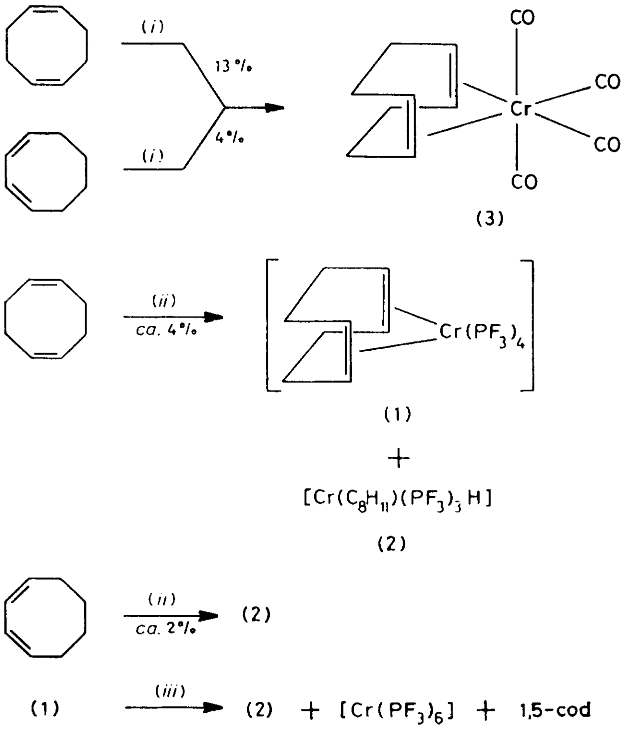
The molecular arrangement of (2) is shown in Figure 1.

TABLE 2

Selected bond lengths (Å) and angles (°)

Cr–P(1)	2.129(3)	P(1)–F(1)	1.516(10)
Cr–P(2)	2.149(3)	P(1)–F(2)	1.546(8)
Cr–P(3)	2.162(3)	P(1)–F(3)	1.590(10)
Cr–C(1)	2.142(9)	P(2)–F(4)	1.552(8)
Cr–C(2)	2.180(9)	P(2)–F(5)	1.596(9)
Cr–C(3)	2.352(10)	P(2)–F(6)	1.524(13)
Cr–C(7)	2.284(11)	P(3)–F(7)	1.548(9)
Cr–C(8)	2.145(10)	P(3)–F(8)	1.491(9)
		P(3)–F(9)	1.543(13)
C(1)–C(2)	1.38(1)	C(5)–C(6)	1.51(2)
C(2)–C(3)	1.44(2)	C(6)–C(7)	1.58(2)
C(3)–C(4)	1.61(2)	C(7)–C(8)	1.37(2)
C(4)–C(5)	1.48(2)	C(8)–C(1)	1.42(2)
P(1)–Cr–P(2)	91.3(1)	Cr–P(1)–F(1)	124.9(4)
P(1)–Cr–P(3)	88.0(1)	Cr–P(1)–F(2)	123.4(3)
P(2)–Cr–P(3)	94.9(1)	Cr–P(1)–F(3)	122.8(4)
Cr–P(2)–F(4)	122.7(4)	F(1)–P(1)–F(2)	87.6(6)
Cr–P(2)–F(5)	119.3(4)	F(1)–P(1)–F(3)	90.4(6)
Cr–P(2)–F(6)	122.3(5)	F(2)–P(1)–F(3)	98.3(5)
F(4)–P(2)–F(5)	91.6(5)	Cr–P(3)–F(7)	121.8(4)
F(4)–P(2)–F(6)	99.5(6)	Cr–P(3)–F(8)	125.3(5)
F(5)–P(2)–F(6)	94.1(6)	Cr–P(3)–F(9)	118.8(6)
C(3)–Cr–C(2)	36.7(4)	F(7)–P(3)–F(8)	92.3(6)
C(2)–Cr–C(1)	37.3(4)	F(7)–P(3)–F(9)	94.4(8)
C(1)–Cr–C(8)	38.8(4)	F(8)–P(3)–F(9)	97.0(7)
C(8)–Cr–C(7)	35.9(4)	C(2)–C(1)–C(8)	128(1)
Cr–C(1)–C(2)	72.8(5)	C(1)–C(2)–C(3)	127(1)
Cr–C(1)–C(8)	70.7(5)	C(2)–C(3)–C(4)	113(1)
Cr–C(2)–C(1)	69.9(5)	C(3)–C(4)–C(5)	116(1)
Cr–C(2)–C(3)	78.2(6)	C(4)–C(5)–C(6)	114(1)
Cr–C(3)–C(2)	65.1(5)	C(5)–C(6)–C(7)	117(1)
Cr–C(8)–C(1)	70.5(5)	C(6)–C(7)–C(8)	123(1)
Cr–C(7)–C(8)	66.5(6)	C(7)–C(8)–C(1)	130(1)
Cr–C(8)–C(7)	77.6(6)		

The chromium atom is linked to five adjacent almost coplanar carbon atoms of the organic ligand. Deviation from planarity of this η^5 system is ± 0.04 Å. Chromium–carbon distances (2.129—2.352 Å) compare well with



SCHEME 1 (*i*) Cr atoms, CO; (*ii*) Cr atoms, PF_3; (*iii*) 90 °C

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

those previously reported for tricarbonyl(cyclo-octa-1,3,5-trienyl)chromium [15] and the dicarbonyl(η^5-pentamethylcyclopentadienyl)chromium dimer.[16] The angles of the conjugated system indicate that a severe strain is forced on the carbon-ring skeleton on complex formation. The non-complexed methylene groups point away from the co-ordination sphere of the central metal atom. One of the two hydrogen atoms positioned near C(3) is close to the chromium atom (1.8 Å). Its position was clear on the difference map mentioned above and is in agreement with the n.m.r. data (see below); this is consistent with a chromium–hydrogen bond.

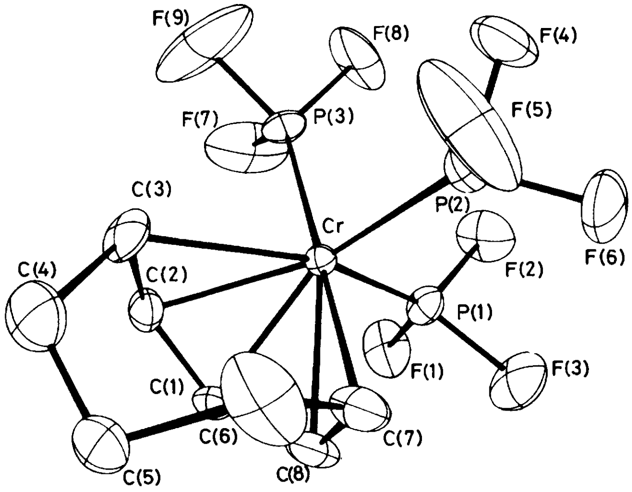

FIGURE 1 *X*-Ray structure of (2)

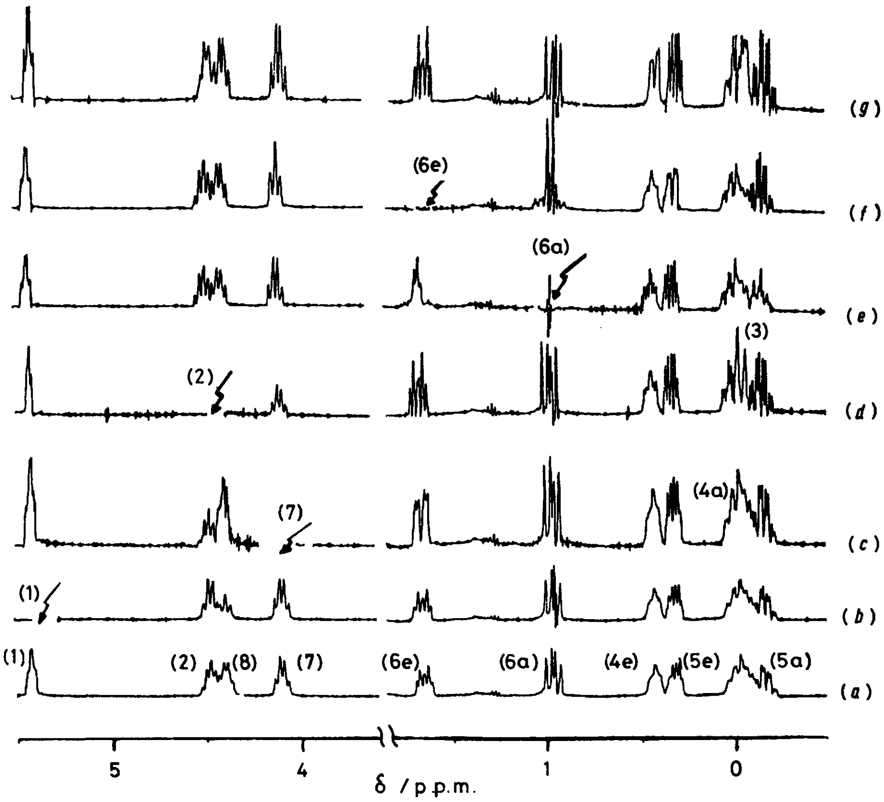

FIGURE 2 400 MHz ^{1}H n.m.r. spectra of the olefinic and methylene protons of (2), $\theta_c = -50$ °C, solvent [$^2H_8$]toluene ($\delta \equiv 2.08$ p.p.m.). (*a*) Normal spectrum, (*b*)—(*g*) double-resonance spectra during decoupling of H(1), H(7), H(2), H(6a), H(6e), and H(Cr) respectively; resolution enhanced spectra by Gaussian transformation

*Hydrogen-*1 *and* ^{13}*C N.M.R. Spectra.*—Complex (2) is soluble and stable in toluene and in chloroform. The low-temperature ^{1}H n.m.r. spectrum (−50 °C, in [$^2H_8$]-toluene) exhibits 12 distinct multiplets (Table 3; Figure 2, the hydride proton at $\delta = -12.58$ p.p.m. is omitted for simplification). The low-field signals at $\delta = 5.42$, 4.47, 4.39, and 4.10 p.p.m. are assigned to the olefinic protons H(1), H(2), H(8), and H(7) respectively, on the basis of the coupling patterns [Figure 2(*a*)] and decoupling experiments. In particular, there is no strong coupling between H(2) and H(8), and irradiation at $\delta = 5.42$ p.p.m. [H(1), Figure 2(*b*)] eliminates a vicinal coupling (*ca.* 8.5 Hz) from the multiplets of H(2) and H(8) but does not cause any other spectral changes. Irradiation at $\delta = 4.10$ p.p.m. [Figure 2(*c*)] demonstrates the vicinity of H(7) and H(8) and the coupling of H(7) with the aliphatic proton at $\delta = 1.64$ p.p.m. [H(6e)]. Irradiation of H(2) [Figure 2(*d*)] not only affects H(1) but also one of the high-field multiplets ($\delta = -0.09$ p.p.m.) which has to be assigned to H(3) on account of its strong coupling with the hydride [^3J(H–Cr–C–H) *ca.* 15 Hz]. In addition, coupling of the hydride occurs with H(2) and H(4e) [^4J(H–Cr–C–C–H) *ca.* 8.5

Hz and 9 Hz respectively] as shown by the spectral changes observed upon irradiation at the hydride position [Figure 2(*g*)]. The positions and couplings of the remaining methylene protons are deduced from decoupling experiments displayed in Figures 2(*e*) and 2(*f*).

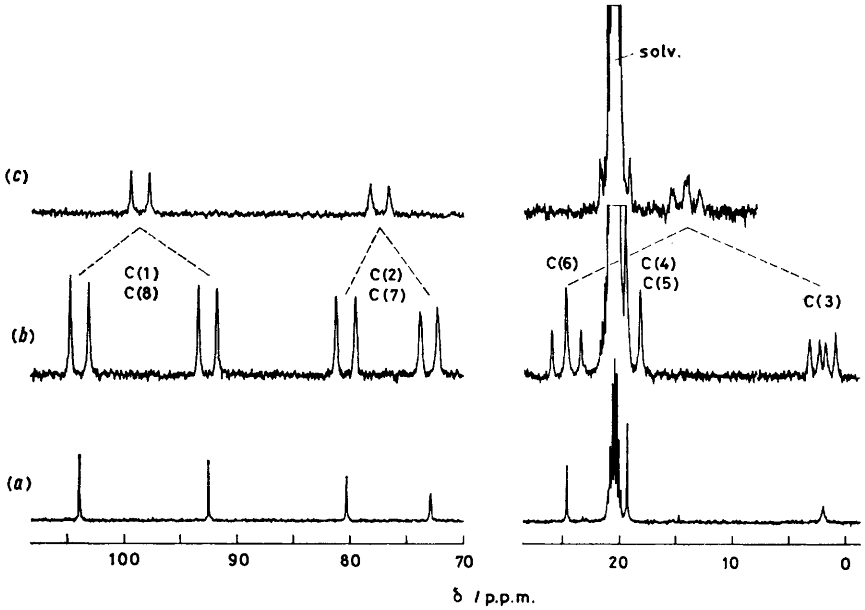

FIGURE 3 100.62 MHz ^{13}C n.m.r. spectra of (2) in [$^2H_8$]toluene (δ = 20.4 p.p.m.). (*a*) Proton noise decoupled spectrum at −80 °C, (*b*) gated decoupled spectrum at −80 °C, (*c*) gated decoupled spectrum at 60 °C (solv. denotes solvent absorption)

The vicinal H,H couplings taken from the low-temperature ^1H n.m.r. spectrum indicate clearly that the structure of (2) in solution is essentially the same as in the solid state. A 1,4- or 1,5-dienyl–metal arrangement can be entirely excluded.

TABLE 3

Hydrogen-1 n.m.r. data for complex (2)

(*a*) Chemical shifts (p.p.m.)

	δ [a] (−50 °C)	δ [a] (60 °C)	δ [b] (140 °C)
H(1)	5.42	5.15	2.70
H(8)	4.39		
H(2)	4.47	4.62	
H(7)	4.10		
H(3)	−0.09	0.94	
H(6e)	1.64		
H(4e)	0.43	0.47	
H(5a)	−0.16		
H(5e)	0.31	0.47	−2.60
H(4a)	0.03		
H(6a)	0.95	−5.70	
H(Cr)	−12.58		

(*b*) Coupling constants (Hz)

J(1,2) = 8.5, *J*(1,8) = 8.5, *J*(1,P) = 5, *J*(2,3) = 8.5, *J*(2,P) = 8.5, *J*(2,H-Cr) = 8.5, *J*(3,4a) = 0, *J*(3,4e) = 4.5, *J*(3,H-Cr) = 15, *J*(4a,4e) = −13.5, *J*(4a,5a) = 13.5, *J*(4a,5e) = 6.4, *J*(4a,H-Cr) = 0, *J*(4e,5a) = 5.4, *J*(4e,5e) = 0, *J*(4e,H-Cr) = 9, *J*(5a,5e) = −13.3, *J*(5a,6a) = 13, *J*(5a,6e) = 0, *J*(5e,6a) = 0, *J*(5e,6e) = 6.4, *J*(6a,6e) = −18.5, *J*(6a,7) = 0, *J*(6e,7) = 8, *J*(7,8) = 9, *J*(7,P) = 8, *J*(8,P) = 8.5.

[a] On a Bruker WH 400 instrument, in [$^2H_8$]toluene. [b] On a Bruker WP 80 instrument, in [$^2H_8$]toluene–[$^2H_{24}$]cyclododecane.

Figure 3 displays (*a*) the proton noise decoupled and (*b*) and (*c*) the gated decoupled ^{13}C n.m.r. spectra of (2) (−80 °C and 60 °C, in [$^2H_8$]toluene; *cf.* Table 4). These spectra complement the ^1H n.m.r. data and show four sp^2 hybridized carbon atoms (δ = 103.9, 92.5, 80.3, and 72.9 p.p.m.), each of which is associated with one proton. Furthermore, two triplets are observed which should correspond to three CH_2 groups; apparently, the signals of C(4) and C(5) at δ = 19.4 p.p.m. are accidentally degenerate.

TABLE 4

Carbon-13 n.m.r. data [a] for complex (2)

	δ (−80 °C)	δ (60 °C)
C(1) or	92.5 (d, 162.8)	98.5 (d, 163)
C(8)	103.9 (d, 163.5)	
C(2) or	80.3 (d, 176.8)	77.3 (d, 164)
C(7)	72.9 (dd, 152.6) [b]	
C(4)	19.4 (t, 128.4)	20.4 (t, 130)
C(5)	19.4 (t, 128.4)	
C(3)	1.9 (dd, 144) [c]	14.0 (dd, *ca.* 105, *ca.* 135)
C(6)	24.7 (t, 131)	

[a] On a Bruker WH 400 instrument, in [$^2H_8$]toluene, multiplicity and ^1J(C,H)/Hz in parentheses. [b] Additional 10 Hz coupling, presumably *J*(C,P). [c] Additional 88 Hz coupling with the hydride proton.

Finally, the highest-field signal appears as a doublet of doublets, *i.e.* this particular carbon atom [C(3)] is strongly coupled not only to the adjacent proton (*J* = 144 Hz) but also to the hydride (*J* = 88 Hz).

From the n.m.r. spectra it becomes evident that the (η^5-cyclo-octadienyl)chromium bonding system of (2) is highly distorted and quite different from ' normal ' (η^5-dienyl)metal complexes, obviously because of the presence of the hydride in close proximity to the C(3)–

H(3) moiety. In particular, $^1J[C(3)-H(3)] = 144$ Hz is somewhat between the values expected for sp^2 and sp^3 hybridized carbon atoms and points towards a significant σ contribution to the Cr–C(3) bond. This should also, at least in part, account for the high shielding of C(3) and H(3) and for the coupling of the hydride proton with C(3), H(3), H(2), and H(4e). Similarly, the ^{1}H and ^{13}C n.m.r. spectra of protonated butadienetricarbonyliron [17] have been interpreted in terms of a σ,η^3-butadieneiron-hydride structure. The assignment of the olefinic and aliphatic carbon atoms (Table 4) is not unambiguous but is supported by variable-temperature spectra (see below) which show the pairwise coalescence of C(1)/C(8), C(2)/C(7), and C(3)/C(6). In agreement with η^4-diene complexes of chromium [18,*] and iron [19] the two lowest-field signals have been assigned to the central atoms of the diene unit, C(1) and C(8); however, the relative assignments of C(1) *versus* C(8) and C(2) *versus* C(7) are still tentative. The resonance at $\delta = 72.9$ p.p.m. shows a splitting of *ca.* 10 Hz which might be due to coupling with one phosphorus atom. Due to a relatively large line width (*ca.* 5 Hz) no further couplings could be observed. The coupling constant $^1J[C(2),H(2)]$ is unexpectedly large and contradicts the generally observed relation $^1J[C(\text{terminal})] < {}^1J[C(\text{central})]$.[18,19] This indicates that the actual bonding situation might be described as a hybrid of a σ,η^4- and a η^5-cyclo-octadienylmetal structure.

Fluxional Behaviour of Complex (2).—A first exchange process can be observed in the ^{13}C n.m.r. (Figure 3, Table 4) and ^{1}H n.m.r. spectra (Figure 4, Table 3) in the temperature range between —80 °C and 60 °C. As mentioned above, C(1)/C(8), C(2)/C(7), and C(6)/C(3) coalesce pairwise such that only four carbon signals [C(4)/C(5) are already accidentally degenerate at low temperature] are observed at the fast exchange limit of this process. Thus, an apparent plane of symmetry bisecting the C(1)–C(8) and C(4)–C(5) bonds is introduced in the molecule on the n.m.r. time scale. This is not merely a matter of ligand–metal bond rearrangements but hydrogen transfer from C(6) to C(3) *via* the metal is also involved. It is H(6a) which points towards the chromium atom and thus can be abstracted by the metal while the original hydride atom is released to C(3). Corresponding changes are observed in the variable-temperature ^{1}H n.m.r. spectra [Figure 4(*a*)—(*d*), Table 3]. Not only H(6a)/H(Cr) and H(3)/H(6e) coalesce pairwise but also H(1)/H(8), H(2)/H(7), H(4e)/H(5a),

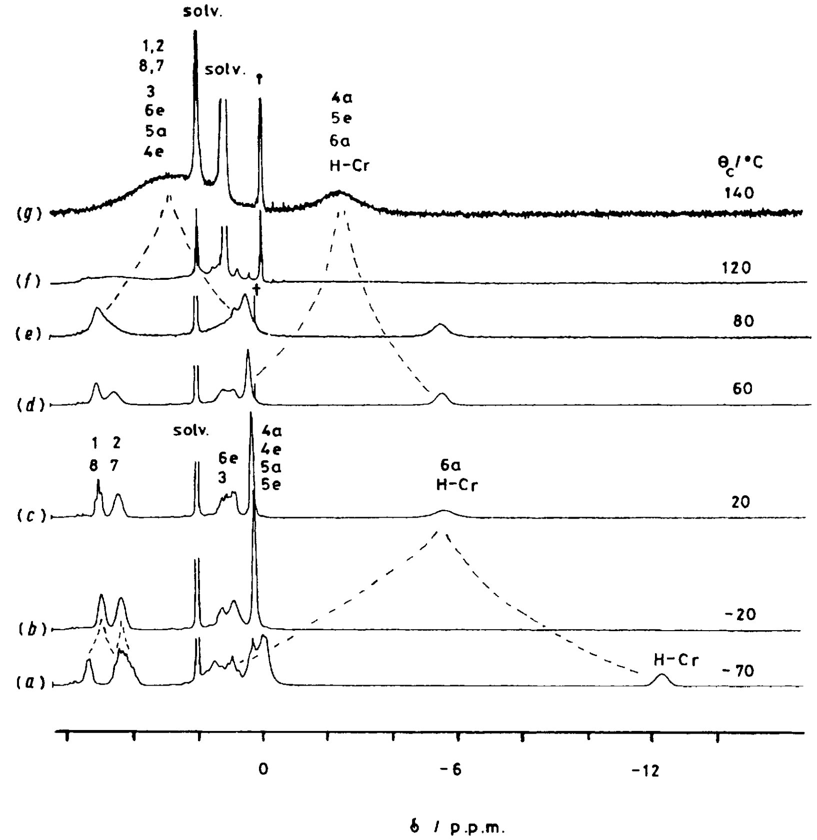

FIGURE 4 80 MHz ^{1}H n.m.r. spectra of (2) at various temperatures, (*a*)—(*e*) in [$^2H_8$]toluene, (*f*)—(*g*) in [$^2H_8$]toluene-[$^2H_{24}$]cyclododecane; solv. denotes the solvent absorptions and a dagger indicates a signal due to silicon grease impurity

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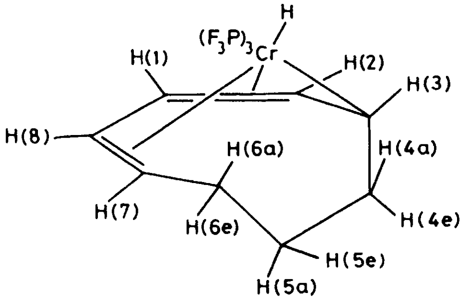
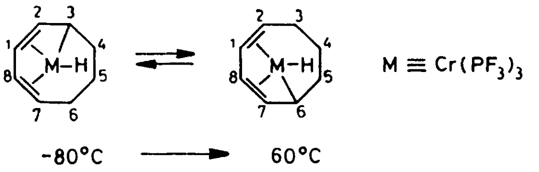
[*] Carbon-13 n.m.r. data on tetracarbonyl(η^4-*trans,trans*-hexa-2,4-diene)chromium:[18] $\delta = 18.0$ [q, ^1J(C–H) *ca.* 130 Hz], 77.8 (d, 158 Hz), 85.7 (d, 164 Hz), 228.2 (s) p.p.m., in [$^2H_8$]toluene at room temperature.

and H(5e)/H(4a), due to the ring rocking about C(4)/C(5). At 60 °C the spectrum [Figure 4(*d*)] exhibits a set of five absorptions with an intensity ratio 2 : 2 : 2 : 4 : 2, since even at 400 MHz the resonances of H(4e)/H(5a) and H(5e)/H(4a) are accidentally degenerate.

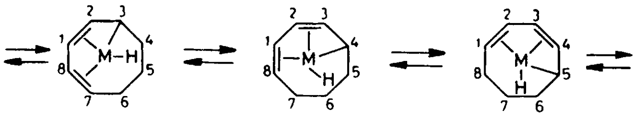
A further fluxional process becomes apparent in the 80 MHz spectra at temperatures above 80 °C [*cf.* Figure 2(*e*)—(*g*)]. As the final result a set of only two broad signals (ratio of integrated intensities 4 : 8) is observed at ⩾130 °C; at 400 MHz this process would require too high temperatures (causing decomposition) or special n.m.r. techniques such as magnetization transfer. Obviously this process involves the coalescence of H(Cr)/H(6a) with H(4a)/H(5e) (four hydrogen atoms) and of the olefinic protons H(1)/H(8), H(2)/H(7) with H(3)/H(6e), H(4e)/H(5a) (eight hydrogen atoms). Both of these two groups of hydrogen atoms coalesce with analogous rates. These spectral changes may again be interpreted in terms of 1,6-hydrogen shifts, however, in contrast to the low-temperature process outlined in Scheme 2, it is now H(4a) which is abstracted by the metal while H(Cr) is released to C(7). Abstraction of H(4a) is sterically less favoured than abstraction of H(6a) and consequently should require a higher activation energy. Continuous repetition of this hydrogen transfer leads the η^5-1,3-dienyl system to rotate around the ring such that the eight ring positions become equivalent. This process involves migration only of H(Cr), H(4a), H(5e), and H(6a), *i.e.* those hydrogen atoms which may point towards the chromium atom. The other eight hydrogens remain attached to their respective carbon atoms throughout. Other mechanisms such as fast exchange reactions involving η^5-1,3-dienyl, η^5-1,4-dienyl, and/or η^5-1,5-dienyl arrangements cannot entirely be excluded. We should, however, favour the mechanism illustrated in Scheme 3 since a series of degenerate rearrangements should exactly average the chemical shifts as is observed within experimental error (*cf.* Table 3).





SCHEME 2

A reaction which is related, at least to some extent, to the fluxional behaviour of complex (2) is the isomerization of tricarbonyl(7-deuteriocycloheptatriene)molybdenum,[20] which was shown to involve exclusive migration of that methylene hydrogen atom which points towards the metal. A metal hydride intermediate, however, was not observed in this case. By contrast, the hydrido-complex (2) is remarkably stable and can be detected over a wide range of temperature.



SCHEME 3

Comparison of the Carbonyl and Trifluorophosphine Systems.—Assuming similar donor capacities of CO and PF_3, and the identical molecular symmetry (C_{2v}) of (1) and (3), the two complexes might be expected to behave similarly in thermally induced rearrangements. The further reaction of (3) to give the carbonyl equivalent of (2) is not, however, observed. A red material with a mass spectrum corresponding to the formula $[Cr(C_8H_{11})(CO)_3H]$ and having an almost identical temperature-dependent ^1H n.m.r. spectrum to (2) has been prepared from photolysis of 1,3-cod and $[Cr(CO)_6]$.[21] The material is, however, not yet fully characterized.

Conclusions.—The variable-temperature n.m.r. spectra of (η^5-cyclo-octa-1,3-dienyl)hydridotris(trifluorophosphine)chromium (2) establish the existence of an exchange between the hydrido-atom and a methylenic hydrogen atom bound to an sp^3 carbon adjacent to a diene unit. Although such C–H bonds are more liable to fission as a result of the particular bonding situation, this C–H interaction-exchange may have a bearing on the activation of alkenes by metal catalysts which often has been proposed to proceed *via* transition-metal hydride intermediates.

The formation of (2) from (1) could be associated with the lability of PF_3 groups co-ordinated to metal diene fragments.[22] Under an atmosphere of PF_3, rearrangement of (1) to (2) is impaired and the 1,5-cod is preferentially replaced by PF_3 to give $[Cr(PF_3)_6]$. Loss of PF_3 from (1) under normal transformation conditions would give a chromium complex having formally 16 electrons in its outer shell; this then undergoes oxidative addition of a C–H bond leading finally, *via* consecutive hydrogen transfer, to the formation of (2).

EXPERIMENTAL

Preparations.— *Tetracarbonyl(η^4-cyclo-octa-*1,5-*diene*)-*chromium* (3). Chromium (400 mg) was co-condensed with cyclo-octa-1,3- or -1,5-diene (40 cm^3) on a pentane matrix (250 cm^3) over 1 h at −196 °C (10^{-4} Torr) in a steel vessel as described previously.[1] The reaction mixture was allowed to warm to room temperature in an atmosphere of CO. The residue, after removal of volatiles, was chromatographed on silica gel (Merck 9385) under argon at 0 °C. The first yellow band was collected and, after removal of solvent, recrystallized from pentane (Found: C, 53.1; H, 4.65; Cr, 18.9. Calc. for $C_{12}H_{12}CrO_4$: C, 52.9; H, 4.45; Cr, 19.1%). Mass spectrum: *m/e* 272 (M^+); 244, 216, 188, and 160 ($M^+ - 1$, 2, 3, or 4 CO). Hydrogen-1 n.m.r. spectrum: δ 3.65 (4), 2.10 (4), and 1.34 (4) p.p.m.

(η^4-Cyclo-octa-1,5-diene)tetrakis(trifluorophosphine)-chromium (1) *and (η^5-cyclo-octa-1,3-dienyl)hydridotris(trifluorophosphine)chromium* (2). Chromium (250 mg) was co-condensed with 1,5-cod (40 cm^3) on a pentane matrix as described above and PF_3 (7 l) was introduced during the warm-up period. A red solution was obtained which, after removal of insoluble material by filtration and evaporation of volatiles, produced a red solid. This was chromatographed on silica gel (Merck 9385) [eluant, n-hexane–diethyl ether (9 : 1)] and the initial red band was collected to yield (2) which was recrystallized from hexane (Found: C, 24.0; H, 2.85; Cr, 12.45; P, 21.95. Calc. for $C_8H_{12}CrF_9P_3$ (2): C, 22.65; H, 2.85; Cr, 12.25; P, 21.9%), *M* (benzene) 437 (calc. 424). Mass spectrum: *m/e* 424 (M^+), 336 ($M^+ - PF_3$), 248 ($M^+ - 2\ PF_3$), 158 ($CrC_8H_{10}^+$), 130, and 52. ^{19}F n.m.r. (30 °C): δ 7.7 (1 F) and 3.9 (2 F) p.p.m., $^1J(PF)$ 1 280 ± 25 Hz.

The second (yellow) band was eluted from the column to yield (1) which was recrystallized from hexane (Found: C, 18.65; H, 2.55; Calc. for $C_8H_{12}CrF_{12}P_4$ (1): C, 18.75; H, 2.35%), *M* (benzene) 572 (calc. 512). Mass spectrum: *m/e* 512 (M^+), 424 ($M^+ - PF_3$), 336 ($M^+ - 2\ PF_3$), 248 ($M^+ - 3\ PF_3$), 160 ($M^+ - 4\ PF_3$), and 106 and 52 (Cr^+). ^1H n.m.r.: δ 3.77 (4 H), 2.10 (4 H), and 1.38 (4 H) p.p.m. ^{19}F n.m.r. (in $CClF_3$): δ 3.33 (2 F) and 11.7 (2 F) p.p.m., $^1J(PF)$ 1 280 ± 25 Hz.

Conversion of (1) *into* (2).—The ^{19}F n.m.r. spectrum of (1) was recorded at 30 °C. The sample was then warmed to 90 °C for 1 h and the ^{19}F n.m.r. spectrum of (2) was recorded at 30 °C. The integrals of the signals established that 3 mol of (1) were converted to 2 mol of (2). The 1,5-cod was isolated and determined quantitatively by gas–liquid chromatography (g.l.c.) (84% of the theoretical quantity was obtained); $[Cr(PF_3)_6]$ was not estimated quantitatively, but the i.r. spectrum of the pentane-insoluble transformation product (in KBr) showed identical stretching frequencies to those obtained from an authentic sample.

Co-condensation of chromium atoms, 1,3-cod, and PF_3 (as described above) produced only (2) after work-up.

Degradation of complexes, followed by g.l.c. analysis, was carried out according to published methods.[23] All the procedures were conducted under argon with solvents which had been dried and distilled under argon by conventional methods.

The ^1H and ^{13}C n.m.r. spectra of complex (2) were recorded with 5-mm and 10-mm sample tubes respectively, in $[^2H_8]$-toluene (−80 to 80 °C) or $[^2H_8]$toluene–$[^2H_{24}]$cyclododecane mixtures (80 to 140 °C) on Bruker WH 400 and WP 80 instruments operating in the Fourier-transform mode. The solvents were purified by distillation from lithium hydride under vacuum. Proton decoupled and gated decoupled ^{13}C n.m.r. spectra could be obtained at 100.62 MHz. Chemical shifts are relative to the methyl signal of $[^2H_8]$-toluene which was used as an internal standard for the ^{13}C (δ ≡ 20.4 p.p.m.) and ^1H n.m.r. spectra (δ ≡ 2.08 p.p.m.) throughout the whole range of temperatures. The spectral changes are reversible as confirmed by recording a spectrum after the sample had been heated to 140 °C.

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