Cycloheptatrienylmolybdenum Complexes. Part 2.[1] Synthesis of Cationic Acetylacetonate Derivatives [Mo(acac)L(η⁷-C₇H₇)]⁺ (L = H₂O, PEt₃, PMe₂Ph, PMePh₂, P(OMe)₃, AsMe₂Ph, or py); Molecular and Crystal Structure of [Mo(acac)(H₂O)(η⁷-C₇H₇)][BF₄]

By **Michael Green, Howard P. Kirsch, F. Gordon A. Stone,*** and **Alan J. Welch,** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The cations $[Mo(CO)_3(\eta^7\text{-}C_7H_7)]^+$ and $[Mo(\eta^6\text{-}C_6H_5Me)(\eta^7\text{-}C_7H_7)]^+$ react with an excess of acetylacetone in dry tetrahydrofuran to form the seventeen-electron aqua-complex $[Mo(acac)(H_2O)(\eta^7\text{-}C_7H_7)]^+$, from which the water molecule may be displaced affording the species $[Mo(acac)L(\eta^7\text{-}C_7H_7)]^+$ (L = PEt₃, PMe₂Ph, PMePh₂, P(OMe)₃, AsMe₂Ph, or py). 1,2-Bis(diphenylphosphino)ethane (dppe) reacts with the aqua-complex to give a dimolybdenum dication $[Mo_2(acac)_2(dppe)(\eta^7\text{-}C_7H_7)_2]^{2+}$. Crystals of the title compound are monoclinic, space group $P2_1/n$, with $a = 8.664(9)$, $b = 18.997(4)$, $c = 9.625(13)$ Å, $\beta = 112.39(8)°$. The structure has been refined to R 0.059 (R' 0.071) for 3 226 independent observed reflections to 2θ 65° (Mo-K_α X-radiation) collected at $ca.$ 215 K. All hydrogen atoms present have been located and positionally and thermally refined.

The crystal structure is built up of two pairs of $[Mo(acac)(H_2O)(\eta^7\text{-}C_7H_7)]^+$ cations and $[BF_4]^-$ anions surrounding a symmetry centre and linked via two independent H $\cdots$ F contacts of 1.84(9) and 2.07(12) Å. The cation features a formally Mo^I metal atom in an approximate octahedral geometry. The tetrafluoroborate counter ion is essentially tetrahedral.

THE complex $[Mo(CO)_3(\eta^7\text{-}C_7H_7)][BF_4]$ reacts with nucleophiles to afford a variety of products, the nature of which depends on the nucleophile and on the stoicheiometry of the reactants. Thus reaction may occur with attack on the cycloheptatrienyl ring to form substituted cycloheptatrienes,[2] removal of the C₇-ring to give complexes of the type $[Mo(CO)_3(fac\text{-}L_3)]$,[2-7] attack on the C₇-ring giving rise to ring contraction affording $[Mo(CO)_3(\eta^6\text{-}C_6H_6)]$,[8] or attack at the metal resulting in substitution of carbonyl groups.[3-5] In order to extend the range of nucleophiles studied we have examined reactions of acetylacetone with the cycloheptatrienyl complexes $[Mo(CO)_3(\eta^7\text{-}C_7H_7)][BF_4]$ and $[Mo(\eta^6\text{-}C_6H_5Me)$-

$(\eta^7\text{-}C_7H_7)][BF_4]$ and have thereby isolated an aqua-compound $[Mo(acac)(H_2O)(\eta^7\text{-}C_7H_7)][BF_4]$ (1). Furthermore, we have found that this complex is a convenient starting material for the synthesis of a number of paramagnetic 17-electron η^7-cycloheptatrienylmolybdenum compounds.[9]

RESULTS AND DISCUSSION

Acetylacetone reacts with $[Mo(CO)_3(\eta^7\text{-}C_7H_7)][BF_4]$ suspended in refluxing tetrahydrofuran to give a yellow-green crystalline complex (1), soluble in dichloromethane and more polar solvents, together with a trace of the

[1] Part 1; M. Bochmann, M. Green, H. P. Kirsch, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 714.

[2] A. Salzer, *Inorg. Chim. Acta*, 1976, **17**, 221.

[3] G. Deganello, T. Boschi, L. Toniolo, and G. Albertin, *Inorg. Chim. Acta*, 1974, **10**, L3.

[4] E. E. Isaacs and W. A. G. Graham, *J. Organometallic Chem.*, 1975, **90**, 319.

[5] K. M. Al-Kathumi and L. A. P. Kane-Maguire, *J.C.S. Dalton*, 1973, 1683.

[6] P. Hackett and G. Jaouen, *Inorg. Chim. Acta*, 1975, **12**, L19.

[7] D. A. Sweigart, M. Gower, and L. A. P. Kane-Maguire, *J. Organometallic Chem.*, 1976, **108**, C15.

[8] J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, 1961, 3479.

[9] M. Bochmann, M. Cooke, M. Green, H. P. Kirsch, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1976, 381.

known [10,11] compound $[Mo_2(CO)_6(\eta^6-C_7H_7)_2]$ (2). The latter is formed in a side reaction since it was observed that when $[Mo(CO)_3(\eta^7-C_7H_7)][BF_4]$ was heated in tetrahydrofuran the di-molybdenum complex was formed.

Complex (1) is more conveniently prepared by refluxing a suspension of $[Mo(\eta^6-C_6H_5Me)(\eta^7-C_7H_7)][BF_4]$ in tetrahydrofuran with acetylacetone. In the i.r. spectrum (1) shows bands in the region 1 600—1 500 cm⁻¹ which may be assigned to the carbonyl groups of an acac ligand. Furthermore, bands in this region suggest that the ligand is bonded through its oxygen atoms rather than through carbon. Bonding as a simple Lewis acid–base adduct in which the acetylacetone bonds through oxygen without loss of its central acidic hydrogen atom is unlikely, as carbonyl stretching frequencies for these complexes generally occur [12,13] nearer 1 700 cm⁻¹. The spectrum of (1) is devoid of terminal carbonyl bands, and absorptions at 3 072, 825, or 795 cm⁻¹ indicate the presence of an η^7-cycloheptatrienyl ring, further suggesting that the acetylacetone moiety is bonded to the metal rather than to the ring.

Previous attempts to substitute completely the CO groups in $[Mo(CO)_3(\eta^7-C_7H_7)][BF_4]$ without removal or substitution at the cycloheptatrienyl ring have generally proved unsuccessful. Indeed, reactions with, for example, $P(OPh)_3$, PPh_3, $AsPh_3$, $SbPh_3$,[4] NCS^-,[14] or halide ions [15] have resulted in the loss of only one carbonyl group. However, in reactions with arenes the CO groups have been completely substituted.[9] Furthermore, attack by acetylacetone at the metal is in contrast to a recent kinetic study [16] involving treatment of
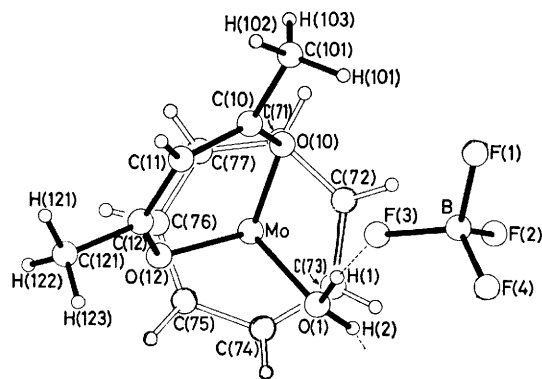

FIGURE 1 View onto the C_7-ring of the complex $[Mo(acac)(H_2O)(\eta^7-C_7H_7)][BF_4]$

$[M(CO)_3(\eta^7-C_7H_7)][BF_4]$ (M = Cr, Mo, or W) with acetylacetone in dichloromethane, leading to reaction at the $\eta^7-C_7H_7$ ring with formation of substituted cycloheptatriene complexes. Under our conditions reaction of acetylacetone with $[Cr(CO)_3(\eta^7-C_7H_7)][BF_4]$ or with $[Cr(\eta^6-C_6H_5Me)(\eta^7-C_7H_7)][BF_4]$ [17] also occurs in a manner

different to that previously described,[16] our major product being $[Cr(acac)_3]$. However, we note that our reactions always involved use of an excess of acetylacetone in refluxing tetrahydrofuran as solvent, and we did observe the presence of a carbonyl containing species in the chromium reaction.

Bands in the i.r. spectrum of (1) in the region 1 200— 1 000 cm⁻¹ were characteristic of the $[BF_4]^-$ anion.

TABLE 1

Bond distances (Å) for the complex $[Mo(acac)(H_2O)(\eta^7-C_7H_7)][BF_4]$ with estimated standard deviations in parentheses

Mo–C(71)	2.256(7)	C(71)–C(72)	1.425(10)
Mo–C(72)	2.291(8)	C(72)–C(73)	1.410(10)
Mo–C(73)	2.268(10)	C(73)–C(74)	1.414(12)
Mo–C(74)	2.277(9)	C(74)–C(75)	1.400(14)
Mo–C(75)	2.257(7)	C(75)–C(76)	1.404(12)
Mo–C(76)	2.248(6)	C(76)–C(77)	1.400(10)
Mo–C(77)	2.255(6)	C(77)–C(71)	1.417(10)
Mo–O(1)	2.202(5)		
Mo–O(10)	2.078(4)	C(71)–H(71)	0.87(6)
Mo–O(12)	2.084(5)	C(72)–H(72)	0.92(7)
		C(73)–H(73)	0.80(8)
O(10)–C(10)	1.296(8)	C(74)–H(74)	0.79(7)
C(10)–C(11)	1.403(9)	C(75)–H(75)	0.85(9)
C(10)–C(101)	1.502(8)	C(76)–H(76)	0.89(12)
C(11)–C(12)	1.394(8)	C(77)–H(77)	0.80(9)
C(12)–O(12)	1.280(9)		
C(12)–C(121)	1.524(13)	C(101)–H(101)	0.99(9)
		C(101)–H(102)	0.98(9)
O(1)–H(1)	0.88(9)	C(101)–H(103)	0.72(9)
O(1)–H(2)	0.71(12)	C(121)–H(121)	1.01(16)
		C(121)–H(122)	0.96(10)
B–F(1)	1.372(11)	C(121)–H(123)	1.02(7)
B–F(2)	1.379(13)	C(11)–H(11)	0.99(10)
B–F(3)	1.391(8)		
B–F(4)	1.368(10)		

Absorptions at 3 373, 3 263, and 1 640 cm⁻¹ were indicative of the presence of a co-ordinated water molecule. This was confirmed by partial deuteriation with D_2O leading to the appearance of bands at 2 461 and 2 414 cm⁻¹. These bands are ca. 100 cm⁻¹ higher than expected for a deuteriated species and this may be caused by H · · · F–B bonding. Since considerable care was taken to exclude all moisture from the reaction we suggest that the water ligand molecule is produced via an aldol condensation of the acetylacetone. The necessity to have an excess of acetylacetone in the reaction if high yields are to be obtained supports this assumption.

In order to clarify the exact nature of (1) a single-crystal X-ray diffraction study was carried out thereby establishing (1) as the ionic complex $[Mo(acac)(H_2O)-(\eta^7-C_7H_7)][BF_4]$.

Neither ion has crystallographically imposed symmetry. Figure 1, the projection of a single cation and its nearest anion onto the plane of the cycloheptatrienyl carbon atoms, demonstrates the atomic numbering

[10] E. W. Abel, M. A. Bennett, R. Burton, and G. Wilkinson, J. Chem. Soc., 1958, 4559.
[11] H. E. Sasse, G. Hoch, and M. L. Ziegler, Z. anorg. Chem., 1974, 406, 263.
[12] J. Lewis, R. F. Long, and C. Oldham, J. Chem. Soc., 1965, 6740.
[13] K. Nakamoto, ' I.R. Spectra of Inorganic and Coordination Compounds,' Wiley, London, 1970, p. 247.
[14] G. Hoch, R. Panter, and M. L. Ziegler, Z. Naturforsch., 1976, 31b, 294.
[15] R. B. King and M. B. Bisnette, Inorg. Chem., 1964, 3, 785, and refs. cited therein.
[16] K. M. Al-Kathumi and L. A. P. Kane-Maguire, J. Organometallic Chem., 1975, 102, C4.
[17] M. Green, H. P. Kirsch, and F. G. A. Stone, unpublished results.

scheme adopted (hydrogen atoms not labelled carry the same number as the carbon to which they are bound). Table 1 lists the bond distances determined, and Table 2 those bond angles not involving hydrogen atoms. Angles involving the latter atoms are deposited.

TABLE 2

Bond angles (°) in the complex [Mo(acac)(H₂O)(η⁷-C₇H₇)]-[BF₄] * with estimated standard deviations in parentheses

Molybdenum co-ordination		Acac ligand	
O(1)–Mo–O(10)	80.2(2)	Mo–O(10)–C(10)	130.6(3)
O(1)–Mo–O(12)	80.9(2)	O(10)–C(10)–C(11)	125.2(5)
O(10)–Mo–O(12)	84.2(2)	O(10)–C(10)–C(101)	114.7(5)
C(71)–Mo–C(72)	36.5(3)	C(11)–C(10)–C(101)	120.1(6)
C(72)–Mo–C(73)	36.0(3)	C(10)–C(11)–C(12)	123.5(7)
C(73)–Mo–C(74)	36.3(3)	C(11)–C(12)–O(12)	125.9(6)
C(74)–Mo–C(75)	36.0(3)	C(11)–C(12)–C(121)	119.1(7)
C(75)–Mo–C(76)	36.3(3)	O(12)–C(12)–C(121)	115.0(6)
C(76)–Mo–C(77)	36.2(3)	C(12)–O(12)–Mo	130.6(4)
C(77)–Mo–C(71)	36.6(2)		

[BF₄]⁻ ion		Cycloheptatrienyl ligand	
F(1)–B–F(2)	107.6(7)	C(77)–C(71)–C(72)	128.7(6)
F(1)–B–F(3)	108.5(6)	C(71)–C(72)–C(73)	127.2(6)
F(1)–B–F(4)	113.1(7)	C(72)–C(73)–C(74)	129.6(7)
F(2)–B–F(3)	110.1(6)	C(73)–C(74)–C(75)	123.8(7)
F(2)–B–F(4)	107.8(7)	C(74)–C(75)–C(76)	128.5(7)
F(3)–B–F(4)	109.7(6)	C(75)–C(76)–C(77)	129.4(7)
		C(76)–C(77)–C(71)	128.3(7)

* Angles involving H atoms are deposited (Appendix B).

The cation is a complex of Mo^I of essentially octahedral geometry in which the η⁷-cycloheptatrienyl group formally occupies three adjacent co-ordination sites and functions as the 6-electron donor C₇H₇⁺.

The carbon atoms of this ligand are co-planar to within 0.008 Å which, together with the small ranges of (i) C–C distances around the ring, 1.400(14)—1.425(10), mean 1.410(9) Å,* and (ii) internal ring angles, 127.2(6)—129.6(7), mean 128.6(8)°, permits the cycloheptatrienyl ligand to be described as essentially a regular, planar heptagon. We have refined the positional and isotropic temperature factors of all hydrogen atoms in the cation and find, without exception, that the cycloheptatrienyl hydrogens lie out of the C₇ plane *on the same side as the metal atom*. This feature of the molecular geometry is further discussed in a following paper.[18]

The molybdenum atom is *ca*. 1.577 Å from the C₇ plane and in projection is only slightly (<0.02 Å) displaced from its centre. Metal–carbon distances [range 2.248(6)—2.291(8), mean 2.265(15) Å] are on average *ca*. 0.054 Å shorter than the corresponding values in [Mo(σ-C₆F₅)(CO)₂(η⁷-C₇H₇)],[19] [Mo(CO)₃(η⁷-C₇H₇)]⁺,[20] [Mo(SnCl₃)(CO)₂(η⁷-C₇H₇)], and [MoX(CO)₂(η⁷-C₇H₇)] (X = Br or Cl),[21] the discrepancy presumably reflecting

* σ_{mean} from $\sigma^2_{mean} = \{ \sum_{i=1}^{N} (\chi_i - \bar{\chi})^2 \}/(N - 1)$ where χ_i is the i'th and $\bar{\chi}$ the mean of N similar $i = 1$ types.

† Use of (i) the Mo–O distance to estimate a Mo^Q+ radius, r, and (ii) the O · · · O bite in the equation, bite = 2.584 + 0.832(r/Q) Å, leads (or, perhaps, misleads) to Q = +2.75 (approx.). A formal oxidation state of Mo^III in (1) necessitates a C₇H₇⁻ 8-electron-donor description for the η⁷-C₇H₇ ring, in contradiction to current ideas on the bonding of this ligand.

the differing oxidation state of the molybdenum atoms in these compounds (all formally Mo⁰) and that in (1).

The atomic sequence Mo,O(10),C(10,11,12),O(12) is planar to within 0.01 Å and subtends a dihedral angle of 60.7° with the C₇-ring. Mo–O(acac) distances agree within 1.5σ and average 2.071 Å. The O(10) · · · O(12) ' bite ' is 2.790(6) Å. These values do not correlate with metal ionic radius and oxidation state in the manner of Lingafelter and Braun,[22,†] although all other molecular parameters fall within the ranges observed for a variety of structures containing the acetylacetonate ligand.

Co-ordination of the metal is completed by the water molecule O(1),H(1),H(2), with Mo–O(1) 2.202(5) Å. The O(1)Mo vector is symmetric with respect to the acetylacetonate ligand [the O(1)–Mo–O(10) and O(1)–Mo–O(12) angles are 80.0(2) and 80.9(2)°, respectively] and produces an elevation angle of 78.1° with the C₇ plane. The three measured angles at oxygen [Mo–O–H 113(5)°, 115(9)°; H–O–H 102(10)°] are reasonable within the limitations on accuracy that accompany X-ray-located hydrogen atoms.

The greatest degree of molecular asymmetry in the cation, at least in the solid state, derives from residence of the water hydrogens on the same side of an approximate mirror plane through O(1), Mo, and C(11). An examination of short intermolecular contacts present in
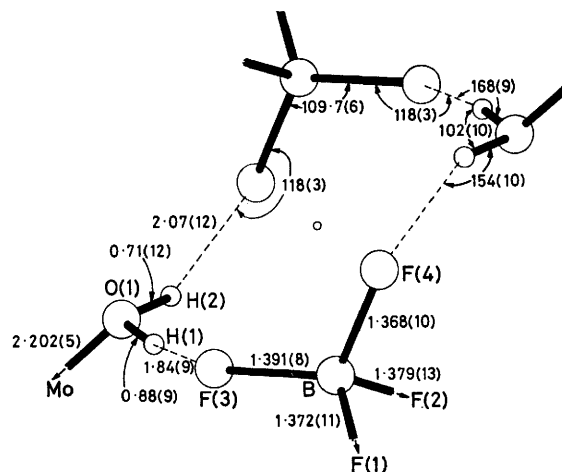

FIGURE 2 Detail of the hydrogen bonding

the crystal structure quickly reveals that both these atoms are involved in hydrogen bonding with different fluorine atoms of related tetrafluoroborate ions. Thus a 12-atom ring, · · ·(· · · HOH · · · FBF · · ·)₂ · · ·, centred about a crystallographic inversion element, is built up (Figure 2).

[18] M. Green, H. P. Kirsch, F. G. A. Stone, and A. J. Welch, to be published.
[19] M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. (A)*, 1969, 1110.
[20] G. R. Clark and G. J. Palenik, *J. Organometallic Chem.*, 1973, 50, 185.
[21] M. L. Ziegler, H. E. Sasse, and B. Nuber, *Z. Naturforsch.*, 1975, 30, 22, 26.
[22] E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, 1966, 88, 2951.

The B–F distances within the anion do not significantly vary, although it is tempting to note that the longest such separation is to F(3), involved in the stronger hydrogen bond. The angles F–B–F span the range 107.6(7)—113.1(7)°. The U_{ii} values reported for the boron atom are probably artificially low, since atomic scattering factors for a neutral atom were used.

The arrangement of ions within one unit cell is reproduced in {0kl} projection in Figure 3. Except for the hydrogen bonding there are no unusually short inter-ligand or inter-molecular contacts.
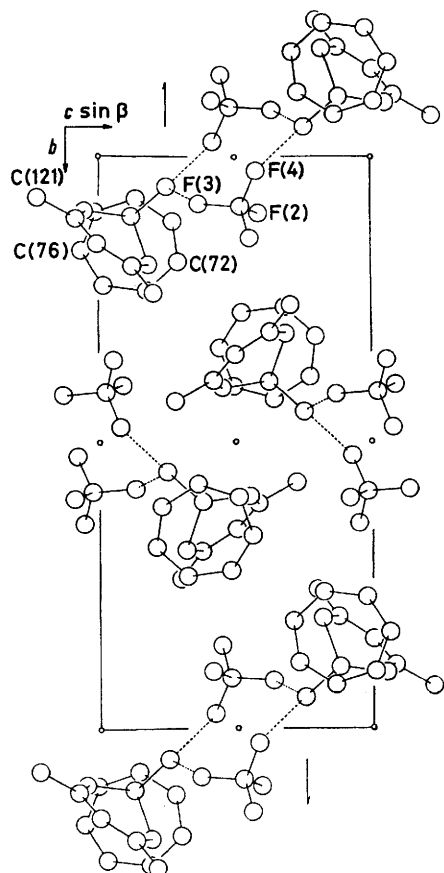

FIGURE 3 Packing diagram in {0kl} projection. Hydrogen atoms are omitted for clarity

The ^{1}H n.m.r. spectrum of (1) showed a broad peak centred at τ 8.43 assignable to the methyl protons of the acac ligand. Chemical shifts for oxygen-bonded acetylacetonate ligands normally lie in the region τ 7.4—8.4.[23] There was no evidence in the spectrum of (1) for protons of the η^7-C$_7$H$_7$ ring, H$_2$O, nor of the central hydrogen atom of the acac ligand near their normal resonance positions, presumably due to paramagnetism.

Magnetic measurements at room temperature show that (1) has a susceptibility of 2.559 × 10^{-6} c.g.s. units,

corresponding to a magnetic moment of 1.63 B.M.* and consistent with one unpaired electron. Similar values have been reported[24] for Mo^I, Mo^{II}, and Mo^{III} complexes.

E.s.r. measurements on (1) are consistent with Mo^I, thus corresponding to a strong-field system, and formally implying C$_7$H$_7^+$ character for the cycloheptatrienyl ligand. The spectrum has a central band at $g = 1.954$ (±0.001) due to the molybdenum isotopes with $I = 0$. No fine coupling was observable on this band. The ^{95}Mo and ^{97}Mo isotopes, which have $I = 5/2$, have similar magnetic moments and coincident resonance lines. Accordingly, the spectrum shows additionally four slightly unsymmetric lines due to these isotopes with a hyperfine coupling $A = 44 \pm 2$ Hz. Presumably, the other two lines due to splitting by these isotopes are hidden under the central band. Furthermore, no fine coupling was observed on the satellite peaks. It is tempting to compare both the g and A parameters with those of related systems. However, this is somewhat dangerous as these values depend[25,26] not only on the donor atoms, but also on the co-ordination number and detailed co-ordination geometry.

Complex (1) is a useful starting material for the synthesis of other η^7-cycloheptatrienylmolybdenum complexes. It reacts readily with group 5A donor ligands with displacement of the water molecule to form the complexes [Mo(acac)(L)(η^7-C$_7$H$_7$)][BF$_4$] [(3), L = PEt$_3$; (4), L = PMe$_2$Ph; (5), L = PMePh$_2$; (6), L = P(OMe)$_3$; (7), L = AsMe$_2$Ph; and (8), L = py]. The i.r. spectra of these complexes are analogous to that of the aqua-compound (1) with absorptions due to the H$_2$O ligand disappearing but being replaced by those of L. The ^{1}H n.m.r. spectra are also similar, no resonances being observed for the C$_7$H$_7$ groups nor for the central hydrogen atom of the acetylacetonate ligand. The spectra were generally weak but broad bands could be assigned to the methyl groups of the acetylacetonate ligand and in some cases to the ligand. The e.s.r. spectra of complexes (3), (4), and (5) are somewhat more complicated than that of complex (1), showing hyperfine coupling associated with the phosphorus nucleus, and further coupling which we tentatively assign to ^{19}F, arising from ion pairing with the [BF$_4$] anion. The spectra of complexes (6) and (8) showed no such hyperfine interaction, but were similar to complex (1).

It is interesting to compare our results with those reported previously involving reactions of η^7-cycloheptatrienylmolybdenum complexes with excess of tertiary phosphines. In none of our reactions do we observe ring displacement, a feature often observed in other studies.[2-7] However, we have observed[27] ring removal in reactions with isocyanides.

Complex (1) reacts with 1,2-bis(diphenylphosphino)-

* 1 B.M. = 0.927 × 10^{-23} A m^2.

[23] J. C. Hammel, J. A. S. Smith, and E. J. Wilkins, *J. Chem. Soc. (A)*, 1969, 1461, and refs. cited therein.

[24] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Interscience, London, 1972, 3rd edn., p. 969.

[25] W. L. Kwik and E. I. Stiefel, *Inorg. Chem.*, 1973, **12**, 2337.

[26] N. Pariyadath, W. E. Newton, and E. I. Stiefel, *J. Amer. Chem. Soc.*, 1976, **98**, 5388.

[27] M. Green, H. P. Kirsch, A. Mortreux, and F. G. A. Stone, unpublished results.

ethane to give the dimolybdenum compound [Mo₂(acac)₂-(dppe)(η⁷-C₇H₇)₂][BF₄]₂ (9). The i.r. spectrum is similar to those of complexes (3)—(8). The n.m.r. spectrum shows a broad band at τ 8.44 due to the methyl groups of the acac ligand and a sharp band at τ 7.82 assigned to the methylene groups of the dppe ligand. The e.s.r. spectrum of (9) is analogous to those of (3)—(5). In view of the spectroscopic similarities it can be assumed that (9) has the same basic structure as the other complexes but with the dppe group bridging two molybdenum atoms.

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 457 spectrophotometer using Nujol and hexachlorobutadiene mulls with KBr plates. N.m.r. spectra were measured on Varian HA-100 and JEOL PFT-100 instruments using CDCl₃ as solvent. The e.s.r. spectra, measured at room temperature (CH₂Cl₂ solutions, ca. 10⁻³ mol dm⁻³), were obtained using a Varian V4502-15 spectrometer (100 kHz field modulation). Diphenylpicrylhydrazyl (g = 2.0037) was used as reference in a dual-cavity arrangement.

Solvents were dried and distilled under nitrogen, and all syntheses were carried out under oxygen-free nitrogen. In particular tetrahydrofuran was dried over sodium benzophenone. Acetylacetone was dried over molecular sieves and then distilled prior to use. The complexes [Mo(CO)₃-(η⁷-C₇H₇)][BF₄],[28] [Mo(η⁶-C₆H₅Me)(η⁷-C₇H₇)][BF₄],[9] [Cr-(CO)₃(η⁷-C₇H₇)][BF₄],[29] and [Cr(η⁶-C₆H₅Me)(η⁷-C₇H₇)] [17] were prepared as described elsewhere.

Synthesis of [Mo(acac)(H₂O)(η⁷-C₇H₇)][BF₄] (1).—(a) *From* [Mo(CO)₃(η⁷-C₇H₇)][BF₄]. A mixture of acetylacetone (1.6 g, 16.1 mmol) and [Mo(CO)₃(η⁷-C₇H₇)][BF₄] (0.6 g, 1.45 mmol) was refluxed in tetrahydrofuran (20 cm³) for 24 h. On cooling and filtering a yellow-green solid was obtained, together with a red-brown filtrate. The solid was recrystallised from an acetone–light petroleum mixture at −23 °C to give yellow-green *crystals* of (1) (0.4 g, 65%), m.p. ca. 170 °C (decomp.) (Found: C, 36.7; H, 4.1. C₁₂H₁₆BF₄MoO₃ requires C, 36.9; H, 4.1%), νmax. 3 373s,br, 3 263m,sh, 3 072m, 3 009m, 2 930w, 2 860w, 1 640w, 1 579s,sh, 1 575s, 1 562s,sh, 1 556vs,sh, 1 551vs, 1 533vs, 1 523vs,sh, 1 510s,sh, 1 441s,sh, 1 435s, 1 354s, 1 291s, 1 253w, 1 199w, 1 181m, 1 158m, 1 115vs, 1 061vs, 1 036vs, 1 021vs, 970s, 953s, 932w,sh, 905w, 876w,sh, 871w, 854w, 825vs, 795s, 777w, 682w, 671w, 590m, 533w, 465m, and 432w cm⁻¹. ¹H N.m.r.: τ 8.43 (br). E.s.r.: central band (g = 1.954 ± 0.001) and four satellites with a further two partially obscured by the central band (Aiso(av.) 44 ± 2 Hz).

The red-brown filtrate was evaporated, the residue was dissolved in dichloromethane, and addition of light petroleum and cooling then afforded red crystals of [Mo₂-(CO)₆(η⁶-C₇H₇)₂], (2) (ca. 50 mg) [Found: C, 43.9; H, 2.7%; M, 537—547 (mass spectrometry). Calc. for C₂₀H₁₄Mo₂O₆: C, 44.3; H, 2.6%; M, 542 (⁹⁶Mo)]. νCO (max.) (CH₂Cl₂ solution): 1 981vs, 1 918vs, and 1 885s cm⁻¹ (lit.,[10,11] 1 994, 1 934, and 1 897; 1 998, 1 929, and 1 898 cm⁻¹).

(b) *From* [Mo(η⁶-C₆H₅Me)(η⁷-C₇H₇)][BF₄]. A green suspension of [Mo(η⁶-C₆H₅CH₃)(η⁷-C₇H₇)][BF₄] (0.5 g, 1.4 mmol), acetylacetone (0.7 g, 7.0 mmol) and tetrahydrofuran (20 cm³) was refluxed for 23 h. On cooling a yellow-

green solid was obtained, which was crystallised to give complex (1) (0.45 g, 81%), identified as above.

Reactions of [Mo(acac)(H₂O)(η⁷-C₇H₇)][BF₄].—(a) *With* D₂O. Complex (1) (114 mg, 0.29 mmol) was dissolved in D₂O (3 cm³) and stirred at room temperature for 17 h. After removal of water *in vacuo* the product was thoroughly dried under high vacuum. An i.r. spectrum of the product showed partial deuteration of the aqua-complex with D₂O bands at 2 461m,br and 2 414m,sh cm⁻¹.

(b) *With* PEt₃. Compound (1) (0.2 g, 0.54 mmol) and triethylphosphine (0.8 g, 6.52 mmol) were refluxed in tetrahydrofuran (10 cm³) for 4 h. After filtration, and washing the filtered residue with diethyl ether, a yellow-green *solid* was obtained which was recrystallised from CH₂Cl₂–Et₂O at −23 °C to give (3) (0.2 g, 68%) (Found: C, 43.4; H, 6.1. C₁₈H₂₉BF₄MoO₂P requires C, 44.0; H, 6.0%). The complex darkens when heated at 145 °C, melting at 173 °C. ¹H N.m.r.: τ 8.39 (br). I.r.: νmax. 3 075w, 2 990m, 2 952m, 2 928vw, 2 896vw, 1 574m,sh, 1 564s,sh, 1 558s, 1 530s, 1 520s, 1 512m,sh, 1 465w,sh, 1 452w, 1 436s,sh, 1 428s, 1 393w, 1 371m, 1 350vs, 1 289m, 1 264w, 1 199w, 1 098s, 1 060vs, 1 039s, 982w, 972vw, 955w, 929w, 905vw, 864w, 826vs, 811m, 780s, 741m, 723w, 589m, 532w, and 458m cm⁻¹.

(c) *With* PMe₂Ph. Complex (1) (0.5 g, 1.28 mmol) and dimethylphenylphosphine (1.4 g, 9.77 mmol) were refluxed in tetrahydrofuran (20 cm³) for 6 h. Filtration and washing of the residue with light petroleum gave yellow-brown *crystals* of (4) (0.5 g, 77%), m.p. ca. 164 °C (decomp.) (Found: C, 47.5; H, 5.1. C₂₀H₂₅BF₄MoO₂P requires C, 47.0; H, 4.9%). ¹H N.m.r.: τ 8.39 (br) and 2.44 (br). I.r.: νmax. 3 062m, 2 992w, 2 922w, 2 858vw, 1 563m,sh, 1 549s, 1 530vs, 1 523s,sh, 1 519s,sh, 1 509m,sh, 1 441s, 1 432s, 1 423s, 1 378m,sh, 1 369m, 1 345s, 1 323w, 1 313m, 1 296s, 1 289s, 1 254m, 1 198w, 1 170w, 1 102s, 1 062vs, 1 046s, 1 005w, 984vw, 971w, 954s, 920s, 903w, 881w, 857w, 843w, 820vs, 804m, 757s, 732w, 707m, 679vw, 584m, 531m, 499m, 457m, and 423w cm⁻¹.

(d) *With* PMePh₂. Complex (1) (0.5 g, 1.28 mmol) and methyldiphenylphosphine (1.0 g, 5.09 mmol) were refluxed (5 h) in tetrahydrofuran (20 cm³). Filtration and washing of the residue with diethyl ether gave dark yellow *crystals* of (5) (0.6 g, 81%), from dichloromethane–diethyl ether at −23 °C, m.p. ca. 155 °C (decomp.) (Found: C, 51.4; H, 4.8. C₂₅H₂₇BF₄MoO₂P requires C, 52.4; H, 4.8%). ¹H N.m.r.: τ 8.16 (br), 2.43 (br), and 1.66 (br). I.r.: νmax. 3 066w, 3 002vw, 2 958w,sh, 2 926m, 2 858w, 1 587w,sh, 1 564m,sh, 1 549vs, 1 535s,sh, 1 525m,sh, 1 509m,sh, 1 489w, 1 442m, 1 428m, 1 372m, 1 350m, 1 345m,sh, 1 323w, 1 303w, 1 288m, 1 198w, 1 190w, 1 178w, 1 099s,sh, 1 050vs, 1 033vs, 1 024s,sh, 997m, 962m, 926w, 897s, 844m, 806vs, 794m, 760s, 751s, 746m, 700s, 516s, 481m, 449m, and 414w cm⁻¹.

(e) *With* Ph₂PCH₂CH₂PPh₂. Complex (1) (0.4 g, 0.97 mmol) and dppe (0.3 g, 0.73 mmol) were refluxed in tetrahydrofuran (20 cm³) for 17 h. Work-up in the usual manner afforded (9) as an orange-green solid (0.5 g, 79%), m.p. ca. 175 °C (decomp.) (Found: C, 52.0; H, 4.6. C₅₀H₅₂B₂-F₈Mo₂O₄P₂ requires C, 52.5; H, 4.6%). ¹H N.m.r.: τ 8.44 (br) and 7.82s. I.r.: νmax. 3 070w, 2 956w,sh, 2 923m, 2 857w, 1 580m,sh, 1 560m,sh, 1 554s,sh, 1 533vs, 1 525vs, 1 509m,sh, 1 482w, 1 443m, 1 439m, 1 431m, 1 423m, 1 362m,sh, 1 343s, 1 320w, 1 289m, 1 196m, 1 175w, 1 113s,sh, 1 082s,sh, 1 058vs,br, 1 036s, 1 028s,sh, 998m,

28 R. B. King, ' Organometallic Syntheses,' vol. 1. 'Transition-metal Compounds,' Academic Press, New York, 1965.

29 J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, 1961, 3475.

966w, 908w, 898w, 874w, 866w, 853m, 814s, 798m, 765s, 763s,sh, 730m, 707s, 686m, 586m, 530s, 496m, 457m, and 451m cm⁻¹.

(f) *With* P(OMe)₃. The complex (1) (0.2 g, 0.51 mmol) and trimethyl phosphite (0.7 g, 7.60 mmol) were refluxed (15 h) in tetrahydrofuran (20 cm³). In this manner (6) was obtained as a dark yellow *solid* (0.2 g, 79%), m.p. 109 °C (decomp.) (Found: C, 36.5; H, 4.9. $C_{15}H_{23}BF_4MoO_5P$ requires C, 36.3; H, 4.7%). ¹H N.m.r.: τ 6.14 (br) and 7.78 (br). I.r.: ν_{max} 3 074w, 2 962m, 2 926w, 2 862w, 1 580m,sh, 1 565vs, 1 556vs, 1 538vs, 1 525vs, 1 515vs, 1 454w, 1 430m, 1 387w, 1 369m, 1 343m, 1 289m, 1 197m, 1 099vs, 1 062vs,br, 1 040vs, 1 027vs, 1 015vs, 974m,sh, 958m, 859m,sh, 839s, 827s, 819s, 804m, 770s, 685m, 593m, 546m, and 465m cm⁻¹. E.s.r.: central band ($g = 1.952 \pm$

1 508m,sh, 1 451s, 1 434m,sh, 1 423m, 1 366m, 1 347s, 1 291s, 1 242w, 1 225m, 1 195w, 1 101s, 1 061vs, 1 042vs,br, 1 018m,sh, 971w, 944w, 901w, 857w, 830vs, 805m, 771s, 702s, 684w, 588m, 527m, and 456m cm⁻¹. E.s.r.: central band ($g = 1.959 \pm 0.001$) and four satellites with hyperfine coupling ($A_{iso(av.)}$ 42 ± 2 Hz).

Reaction of $[Cr(CO)_3(\eta^7\text{-}C_7H_7)][BF_4]$ *with Acetylacetone.*— The complex $[Cr(CO)_3(\eta^7\text{-}C_7H_7)][BF_4]$ (0.2 g, 0.64 mmol) and acetylacetone (3.0 g, 30.0 mmol) were suspended in tetrahydrofuran (8 cm³) and refluxed for 21 h. A red solution was obtained, which was evaporated. Extraction with light petroleum gave a red solution from which a pure product could not be obtained. An i.r. spectrum showed ν_{CO} (max.): 1 984vs, 1 922vs, and 1 900vs cm⁻¹. Extraction with diethyl ether of the solid remaining after light-

TABLE 3

Final positional (fractional co-ordinate, × 10⁴; Mo, × 10⁵) and anisotropic * thermal (Å², × 10⁴; Mo, × 10⁵) parameters of the non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	13 882(5)	13 614(2)	12 089(5)	1 402(35)	1 659(33)	1 864(34)	−11(17)	741(17)	−140(17)
O(1)	3 142(6)	540(2)	2 496(6)	213(20)	263(21)	319(22)	16(16)	58(18)	63(18)
O(10)	3 623(5)	1 912(2)	1 838(4)	178(17)	207(17)	268(19)	−21(14)	107(15)	−21(15)
C(10)	4 734(6)	1 929(3)	1 242(6)	140(21)	162(21)	272(24)	19(17)	69(19)	66(18)
C(11)	4 653(8)	1 548(3)	−32(7)	276(28)	263(27)	330(28)	25(22)	174(25)	39(22)
C(12)	3 342(7)	1 097(3)	−819(7)	255(26)	249(25)	294(26)	25(21)	160(22)	−9(21)
O(12)	2 075(5)	962(2)	−489(5)	249(19)	244(19)	268(19)	−26(16)	138(16)	−79(16)
C(101)	6 195(7)	2 404(4)	2 026(8)	161(24)	267(28)	368(32)	−79(22)	88(23)	0(25)
C(121)	3 352(12)	726(5)	−2 220(10)	547(48)	501(47)	493(44)	−139(38)	378(41)	−257(37)
C(71)	342(7)	2 358(3)	1 780(8)	193(24)	200(24)	418(32)	6(20)	126(24)	−73(23)
C(72)	474(8)	1 859(4)	2 926(7)	259(28)	434(35)	196(24)	57(25)	133(22)	−26(23)
C(73)	−14(9)	1 146(4)	2 731(9)	335(33)	409(35)	411(35)	105(27)	277(29)	158(29)
C(74)	−798(10)	758(4)	1 391(11)	368(36)	193(28)	902(64)	−70(26)	419(42)	−22(33)
C(75)	−1 240(8)	986(4)	−94(9)	198(27)	436(39)	528(42)	−74(27)	132(28)	−250(35)
C(76)	−1 055(8)	1 658(4)	−618(7)	202(27)	571(43)	227(26)	102(28)	49(22)	−70(28)
C(77)	−362(8)	2 268(4)	199(7)	213(26)	327(31)	321(29)	48(23)	111(23)	88(25)
B	7 265(11)	879(4)	5 223(8)	442(40)	249(30)	256(29)	−35(29)	90(29)	59(25)
F(1)	8 330(10)	1 445(4)	5 544(6)	1 300(59)	832(44)	469(28)	−759(44)	135(33)	−52(29)
F(2)	6 124(9)	1 003(4)	5 877(7)	959(46)	814(41)	691(37)	247(36)	549(36)	44(31)
F(3)	6 453(5)	829(2)	3 671(4)	309(19)	463(23)	291(17)	14(17)	50(15)	−12(16)
F(4)	8 058(8)	259(3)	5 784(7)	782(39)	641(35)	798(39)	393(30)	333(32)	410(31)

* Defined as $\exp\{-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)\}$.

0.001) and four satellites with a further two obscured by the central band ($A_{iso(av.)}$ 44 ± 2 Hz).

(g) *With* AsMe₂Ph. Similarly, (1) (0.2 g, 0.51 mmol) and dimethylphenylarsine (1.2 g, 6.59 mmol) in tetrahydrofuran (10 cm³) after reflux (6 h) gave yellow solid (7) (0.14 g, 49%), m.p. *ca.* 152 °C (decomp.) (Found: C, 42.0; H, 4.5. $C_{20}H_{25}AsBF_4MoO_2$ requires C, 43.3; H, 4.5%). ¹H N.m.r.: τ 6.23 (br) and 8.13 (br). I.r.: ν_{max} 3 071w, 2 928w, 2 857vw, 1 582m,sh, 1 572m,sh, 1.560s,sh, 1 553vs, 1 532vs, 1 523vs,sh, 1 513m,sh, 1 442m,sh, 1 435m, 1 354vs, 1 323w, 1 290m, 1 278w, 1 263w, 1 200w, 1 196w, 1 106s,sh, 1 095s, 1 062vs,sh, 1 053vs, 1 042vs, 1 029s,sh, 1 004m,sh, 973m,sh, 968m, 955w, 917m, 886m, 863w, 830s, 824m,sh, 804m, 795m, 763m, 756m, 708m, 680w, 587m, 555w, 533m, 485m, and 456m cm⁻¹.

(h) *With* C₅H₅N. Similarly, (1) (0.49 g, 1.25 mmol) and pyridine (10 cm³) were refluxed (4.5 h) to give yellow-green *solid* (8) (0.42 g, 74%), m.p. *ca.* 150 °C (decomp.) (Found: C, 45.9; H, 4.7; N, 3.5. $C_{17}H_{19}BF_4MoNO_2$ requires C, 45.2; H, 4.2; N, 3.1%). ¹H N.m.r.: τ 1.25 (br), 2.54 (br), and 7.96 (br). I.r.: ν_{max} 3 068m, 2 958w, 2 922w, 2 852w, 1 606m, 1 571m,sh, 1 562vs, 1 533s, 1 523m,sh, 1 518s,

petroleum treatment gave red-purple crystals (0.23 g, 94%), from light petroleum at −23 °C, of [Cr(acac)₃] (Found: C, 51.4; H, 6.3. Calc. for $C_{15}H_{21}CrO_6$: C, 51.6; H, 6.1%). The i.r. spectrum was identical with that of an authentic sample.

X-Ray Crystallographic Study.—A single crystal, *ca.* 0.25 × 0.20 × 0.15 mm, was mounted on a glass fibre with low-temperature epoxy-resin adhesive and aligned on a Syntex *P*2₁ four-circle diffractometer equipped with a φ-axis cooling device [30] set to produce a localised crystal temperature of *ca.* 215 K.

Fifteen reflections, 9 < 2θ < 22° (Mo X-radiation), were taken from the rotation photograph (30 m) and centred in 2θ, ω, and χ; axial vectors were chosen to correspond to a primitive monoclinic cell previously defined by oscillation and equi-inclination Weissenberg photography.

One asymmetric set of diffracted intensities was recorded as previously described.[31] Details pertinent to the present experiment include: 2.9 ⩽ 2θ ⩽ 65.0°; Mo-K_α radiation ($\lambda_{\alpha 1}$ 0.709 26, $\lambda_{\alpha 2}$ 0.713 54 Å); θ—2θ scan in 96 steps at rates between 0.033 67 and 0.488 33° s⁻¹ according to an initial 2-s peak count in which 100 and 2 000 were used as critical values; the intensities of 3 check reflections ($\bar{1}3\bar{1}$,

30 R. J. Goddard, S. D. Killops, S. A. R. Knox, and P. Woodward, *J.C.S. Dalton*, to be submitted.

31 A. G. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

341, and 151) were monitored once every 35 reflections but showed [32] no significant variation over the *ca.* 157-h X-ray exposure. Of 3 461 independent reflections measured, 3 226 had $I \gg 1.0\sigma(I)$ and were retained for structure solution and refinement.

Crystal Data.—$[C_{12}H_{16}MoO_3][BF_4]$, $M = 391.00$, Monoclinic, space group $P2_1/n$, $a = 8.664(9)$, $b = 18.997(14)$,

TABLE 4

Hydrogen atom positional (fractional, $\times 10^3$) and isotropic thermal ($Å^2$, $\times 10^3$) parameters with estimated standard deviations in parentheses

Atom	x	y	z	U_j *
H(1)	418(11)	69(4)	291(9)	34(21)
H(2)	300(13)	41(6)	313(12)	52(31)
H(11)	559(10)	158(4)	−38(8)	30(20)
H(101)	677(11)	220(5)	304(11)	44(24)
H(102)	686(9)	241(4)	140(8)	18(16)
H(103)	589(10)	276(5)	200(9)	28(21)
H(121)	419(16)	94(7)	−259(14)	85(38)
H(122)	223(15)	69(6)	−294(12)	62(31)
H(123)	345(8)	20(4)	−200(7)	16(16)
H(71)	93(8)	273(4)	220(7)	14(15)
H(72)	118(9)	199(4)	388(9)	25(18)
H(73)	26(9)	93(4)	350(8)	22(17)
H(74)	−92(8)	35(4)	147(7)	13(15)
H(75)	−146(11)	65(5)	−72(10)	42(23)
H(76)	−102(12)	172(5)	−153(12)	56(28)
H(77)	−24(9)	258(4)	−31(9)	24(18)

* Defined as $\exp\{-8\pi^2 U_j(\sin^2\theta)/\lambda^2\}$.

$c = 9.625(13)$ Å, $\beta = 112.39(8)°$, $U = 1\,465(2)$ Å^3, $D_c = 1.772$ g cm^{-3}, $Z = 4$, $D_m = 1.78$ g cm^{-3}, $F(000) = 780$, $\mu(Mo\text{-}K_{\bar{\alpha}}) = 9.9$ cm^{-1}.

Data were corrected for Lorentz and polarisation effects but not for X-ray absorption. The position of the molybdenum atom was easily deduced from a Patterson synthesis, and used to calculate the first set of phases. Although non-hydrogen atoms were located from subsequent electron-

density difference-Fouriers calculated with the entire data set, the technique [33] of including only those (1 365) data with $\sin\theta \geqslant 0.5\lambda$ in ΔF syntheses was employed to 'find' the hydrogens.

Weights were applied according to $w^{-1} = x \cdot y$ with $x = 0.22/\sin\theta$ if $\sin\theta < 0.22$, $x = 1$ if $\sin\theta \geqslant 0.22$, and $y = F_0/75$ if $F_0 > 75$, $y = 1$ if $F_0 \leqslant 75$.

With the (258) variables divided between two blocks [(A), $4 \times F$ scale factors, overall temperature factor, Mo and C_7H_7 parameters; (B), acac, OH_2 and BF_4 parameters], mixed refinement (non-hydrogen atoms anisotropic) continued until the maximum shift-to-error on any one variable was $<0.05 : R\ 0.059$ ($R'\ 0.071$). The largest residue on a final difference-Fourier (all data) was *ca.* 1.1 eÅ^{-3} (coordinates 0.18, 0.44, 0.11).

Atomic scattering factors for neutral atoms were taken from ref. 34 for molybdenum, fluorine, and boron, ref. 35 for carbon and oxygen, and ref. 36 for hydrogen, with appropriate correction for anomalous dispersion.[37]

Tables 3 and 4 list the derived atomic positional and thermal parameters. Appendix A compares F_0 with F_c at the conclusion of refinement, B lists those bond angles involving hydrogen atoms, and C contains details of molecular planes. All Appendices are contained within Supplementary Publication No. SUP 22057 (16 pp.).* The solution and refinement of the structure employed programs of the 'X-Ray '72' crystallographic computing package,[38] implemented on the University of London CDC 7600 machine.

We thank Dr. J. Maher for assistance in measurements and interpretation of the e.s.r. spectra, Dr. K. S. Murray for magnetic measurements, and Mr. R. Carson for data on the reaction of acetylacetone with cycloheptatrienyl-(toluene)chromium tetrafluoroborate.

* See Notice to Authors No. 7 in *J.C.S. Dalton,* 1976, Index issue.

[32] A. G. Modinos, DRSYN, a Fortran program for data analysis.

[33] M. R. Churchill and B. G. DeBoer, *J. Amer. Chem. Soc.,* 1974, **96**, 6310.

[34] D. T. Cromer and J. T. Waber, *Acta Cryst.,* 1965, **18**, 104.

[35] D. T. Cromer and J. B. Mann, *Acta Cryst.,* 1968, **A24**, 321.

[36] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.,* 1965, **42**, 3175.

[37] 'International Tables for X-Ray Crystallography,' vol. IV, Kynoch Press, Birmingham, 1974.

[38] Technical Report TR–192 of the Computer Science Centre, University of Maryland, June 1972.