Reactivity of Co-ordinated Ligands. Part XVII.[1] Heptafulvene Complexes of Chromium, Molybdenum, and Tungsten

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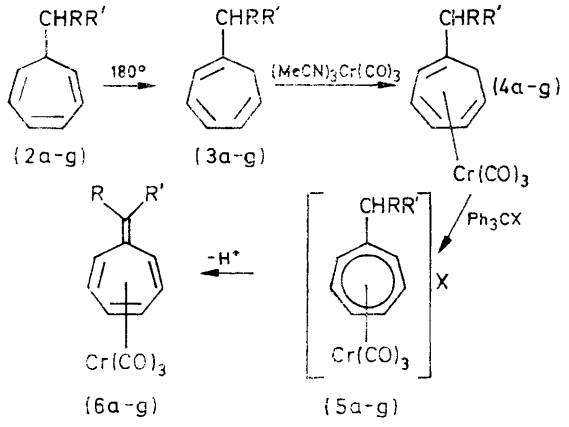
Heptafulvene complexes of tricarbonylchromium, $RR'C_8H_6Cr(CO)_3$ (R = H, R' = H, Me, or Ph; R = Me, R' = Me or Et; R = Ph, R' = Me or Ph), tricarbonylmolybdenum $RR'C_8H_6Mo(CO)_3$ (R = Ph, R' = Me or Ph), and tricarbonyltungsten $RR'C_8H_6W(CO)_3$ (R = Me, R' = Et; R = Ph, R' = Me or Ph) have been prepared. Their reactivity towards electrophilic reagents has been investigated and is different to that of the analogous derivatives of tricarbonyliron. Thus whereas addition or substitution occurs on the ring system of the iron complexes these complexes resemble free heptafulvenes in showing exclusive reactivity at the exocyclic double bond. The complexes function as a convenient source of the reactive heptafulvene for *in situ* reactions with dienophiles.

RECENT work in this laboratory,[2] has led to the synthesis of tricarbonyliron complexes of the reactive and unstable heptafulvene (I) and its 8-substituted derivatives. A study of their chemical reactivity has revealed that in contrast to free heptafulvenes, where attack occurs on the exocyclic carbon atom, electrophilic substitution and addition occurs on the ring system. However, contrary



(a) R = Ph, R' = Me;
(b) R = R' = Ph;
(c) R = Me, R' = Et;
(d) R = R' = Me;
(e) R = H, R' = Me;
(f) R = H, R' = Ph;
(g) R = R' = H.

SCHEME

to expectations, the iron complexes do not serve as a source of free heptafulvene for reactions *in situ* in a manner similar to that employed for cyclobutadiene from tricarbonyl(cyclobutadiene)iron,[3] and all attempts to liberate the heptafulvene by oxidation of the complex are accompanied by oxidation of the ligand. The complexes themselves remain unreactive towards dienophiles even at elevated temperature (except for tetracyanoethylene, in which case the metal remains co-ordinated).[4]

The ready displacement of the ligand from tricarbonyl(cycloheptatriene)chromium by arenes [5] suggested that the analogous, but unknown, chromium compounds might have more synthetic potential. To this end, a number of heptafulvene complexes of Cr, Mo, and W have been synthesised. Part of this work has been reported in a previous communication.[6]

TABLE 1

Tropylium complexes

Complex	Chemical shift (τ) [a] Ring protons	Substituent	I.r. spectral data [b]
(5a)	3·47	CH (q) 5·62 CH_3 (d) 8·27 Ph, 2·64 (m)	2023, 2067
(5b; X = BF_4^-, PF_6^-)	*c*		2023, 2071
(5c)	3·14	CH, 6·93 (quintet) CH_3, 8·48 (d) *J* 6·8 Hz CH_2, 8·20 (m) } *J* 6·8 Hz CH_3, 8·94 (t) }	2022, 2063
(5d; X = BF_4^-, PF_6^-)	3·43	CH, 6·77 (sept) *J* 7·3 Hz $2CH_3$, 8·54 (d)	2021, 2066
(5e)	3·60	CH_2, 8·05(q) } CH_3 (t) 8·58 } *J* 7·0 Hz	2023, 2068
(5f)	3·50	Ph (s) 2·62 CH_2 (s) 5·78	2028, 2072
(5g; X = PF_6^-, BF_4^-)	3·58	CH_3 (s) 7·71	2019, 2066
(13a)	3·87	CH (q) 5·82 } CH_3 (d) 8·33 } *J* 7·2 Ph (s) 2·68	2037, 2088
(13b)		*c*	2032, 2083
(14a)	3·91	CH (q) 5·76 } CH_3 (d) 8·32 } *J* 7·1 Ph (s) 2·67	2011, 2073
(14b)		*c*	2013, 2074
(14c)	3·86	CH (quintet) 7·29 CH_3 (d) 8·69, *J* 7·1 Hz CH_2 (m) 8·35 } CH_3 (t) 9·04 } *J* 6·8 Hz	
(19)	4·07	PPh_3 (m) 2·45 Ph (s) 2·68 CH_2 (s) 5·82	1978, 2006

[a] CD_3CN Solution. [b] ν(CO), In cm^{-1}, CH_2Cl_2 solution. [c] Decomposes in CD_3CN.

Syntheses.—The syntheses of the new tricarbonyl(heptafulvene)chromium complexes were accomplished by the route shown in the Scheme. The precursor compounds, the 7-substituted cycloheptatrienes (2a—g) were

[1] Part XVI, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1974, 145.
[2] B. F. G. Johnson, J. Lewis, P. McArdle, and G. L. P. Randall, *Chem. Comm.*, 1971, 177; *J.C.S. Dalton*, 1972, 2076.
[3] L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, 1965, **87**, 3253.
[4] P. McArdle, personal communication.
[5] J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, 1961, 3475.
[6] J. A. S. Howell, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1972, **42**, C54.

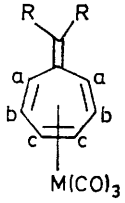
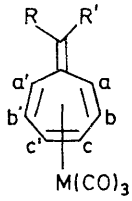
prepared by the reaction of either tropylium tetrafluoroborate or 7-ethoxycycloheptatriene with the appropriate lithium alkyl or Grignard reagent. Thermal isomerization of these derivatives gave predominantly the 1-isomers (3a—g) which were easily identified by the characteristic methylenic doublet observed in their ^1H n.m.r. spectra. This isomerization was necessary in some cases because the free compounds (2a—c) do not react with Ph_3CBF_4 presumably because of steric hindrance about the 7-carbon atom. The free ligands (2d—g) react readily, as do the 1-isomers produced on isomerization.

The i.r. spectra exhibit three absorptions typical of tricarbonyl(cycloheptatriene)chromium complexes.[7a] The mass spectra show a parent ion, followed by stepwise loss of three CO's and chromium. The n.m.r. spectra clearly show the symmetric co-ordination of the tricarbonylchromium group to the triene system [*e.g.* the singlet obtained for the methyl resonance of (6d)] and there is therefore no possibility of isomerism or fluxionality as observed in the corresponding iron complexes.[2]

The monosubstituted complexes (6e—f) and the parent complex (6 g) have not been isolated as pure compounds. They are considerably less stable than the analogous iron complexes, and decompose under the purification conditions used for the disubstituted chromium complexes. However, mass spectral and i.r. evidence, as well as reactions to be discussed later, show that they are produced in the reaction sequence.

TABLE 2

Heptafulvene complexes

	Complex	Chemical shift (τ) [a] Ring protons	Substituent, R	I.r. spectral data [b]	P^+ (*m/e*) [c]
	(6b)	Ha, Hb (m) 5·60 Hc (m) 4·24	Ph (m), 2·86	1993, 1938, 1912	392
	(6d)	Ha (d) 5·92, *J* 9·6 Hz Hb (m) 5·36 Hc (m) 4·22	Me (s) 8·44	1985, 1931, 1905	268
	(15b)	Ha, Hb (m) 5·36 Hc (m) 4·36	Ph (m) 2·97	1990, 1931, 1902	436
	(6e)	*d*		1983, 1926, 1904	254
	(6f)	*d*		1987, 1935, 1912	316
	(6g)	*d*		1980, 1920, 1898	240
	(16a)	*d*		1988, 1920, 1888	462
	(16c)	*d*		1983, 1917, 1886	414
	(6a)	Ha(a'), 5·84 (d) *J* 10·0 Hz Ha'(a), 5·87 (d) *J* 10·0 Hz Hb(b'), 5·27 (m) Hb' (b), 5·58 (m) Hc, c', 4·21 (m)	Me, 8·11 (s) Ph, 2·89 (m)	1996, 1941, 1911	330
	(6c)	Ha(a'), 5·82 (d) *J* 9·7 Hz Ha'(a), 5·91 (d) *J* 9·7 Hz Hb,b', 5·40 (m) Hc,c', 4·22 (m)	CH_3 (s) 8·46 CH_2 (q) 8·06} CH_3 (t) 9·13,} *J* 7·2 Hz	1992, 1942, 1909	282
	(15a)	Ha,a' (m) 5·55 Hb,b' (m) 5·24 Hc,c' (m) 4·33	Me, 8·08 (s) Ph, 2·90 (m)	1998, 1941, 1910	374

[a] CS_2 Solution. [b] ν(CO), In cm^{-1}, cyclohexane solution. [c] Based on ^{52}Cr, ^{96}Mo, and ^{184}W. [d] Not sufficiently stable.

Treatment of the compounds (3a—g) with $(MeCN)_3Cr(CO)_3$ in tetrahydrofuran gave the tricarbonyl(cycloheptatriene)chromium complexes (4a—g). Subsequent reaction of these complexes with Ph_3CBF_4 [or Ph_3CSbF_6 in the case of 4(a)] yielded the tricarbonyl(tropylium)-chromium salts (5a—g) (see Table 1). Proton abstraction with the strong, non-nucleophilic base 1,8-bis-(dimethylamino)naphthalene gave the deep red tricarbonyl(heptafulvene)chromium derivatives (6a—g) (see Table 2). These compounds have been assigned the structure shown on the basis of elemental analysis, and ^1H n.m.r., i.r., and mass spectroscopic data.

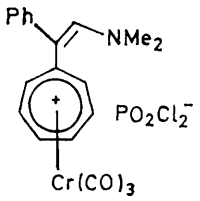
Reactions with Electrophilic Reagents.—The co-ordination of the third double bond of the ring results in a significant change in the reactivity of the heptafulvene towards electrophilic reagents. Thus, whereas addition

[7] (*a*) E. O. Fischer and H. Werner, 'Metal π-Complexes,' vol. 1, Elsevier, 1966, p. 88; (*b*) C. Jutz, *Chem. Ber.*, 1964, **97**, 2050.

or substitution occurs on the ring system of the iron complexes,[2] the chromium compounds resemble free heptafulvenes [7b] in showing exclusive reactivity to electrophilic reagents at the exocyclic double bond. For example, protonation of (6b,d) with HPF_6 regenerates the tricarbonyl(tropylium)chromium cations (5b,d). Similarly, protonation of the parent compound (6 g) gives a 30% recovery of the tricarbonyl(methyltropylium)chromium cation, indicating a conversion to the heptafulvene complex of at least this yield in the deprotonation reaction of the Scheme.

Substitution reactions may be performed only on the monosubstituted complexes (6e—g), as compounds (6a—d) are already fully alkyl- or aryl-substituted at the 8-carbon atom.

Attempted formylation of (6f) with $POCl_3$–DMF or oxalylchloride–DMF leads to formation (in solution) of an ionic intermediate formulated as (7), but hydrolysis does



(7)

not give the expected aldehyde. Instead of elimination to reform the double bond, a complex mixture of products is formed, most probably resulting from hydrolytic attack on the tropylium cation.

Neither the parent complex (6g) nor the disubstituted complex (6c) show any reactivity to $Et_3O^+BF_4^-$. The preference for electrophilic attack at the exocyclic olefinic bond may be attributed to the stability of the tricarbonyl(tropylium)chromium cation, either as an intermediate, or as the final product. Electron deficient tricarbonyl(dienyl)chromium cations, analogous to the very stable and well characterized tricarbonyl(dienyl)-iron cations,[8] are unknown. On the other hand, although the tricarbonyl(tropylium)iron cation is known,[9] it is less stable than the free tropylium ion, and considerably less stable than the tropylium complexes of chromium, molybdenum, and tungsten.

Reaction with Dienophiles.—These complexes have been found to act as sources of the heptafulvene in *in situ* reactions with dienophiles. However, the mechanism appears to be dissociative, involving loss of the $Cr(CO)_3$ group, rather than displacement of the heptafulvene by the arene.

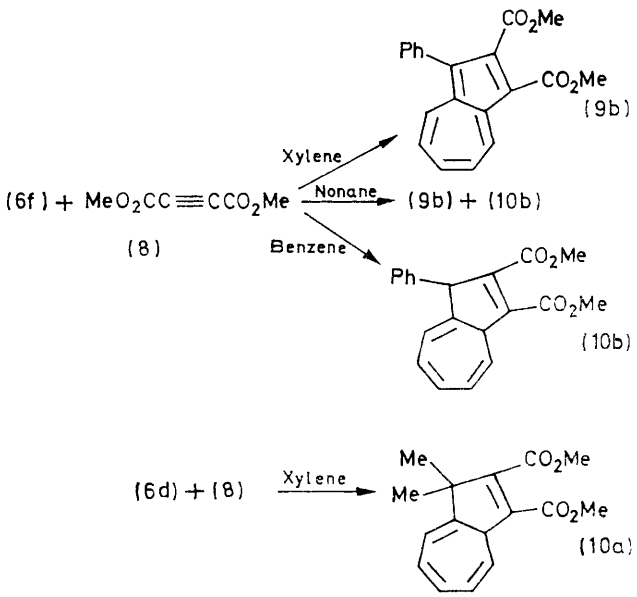
Reaction of dimethylacetylene dicarboxylic ester (8) in refluxing xylene gave, for the monosubstituted compounds (6e—g) the azulene derivatives (9a—c), formed by dehydrogenation of the initially formed Diels–Alder adducts at the temperature of refluxing xylene. For the disubstituted compound (6d), where such dehydrogenation is not possible, the Diels–Alder adduct (10a) was obtained.

Tricarbonyl(xylene)chromium was not detected. Furthermore if the above reaction, using (6f), is carried out in n-nonane for half the length of time, a mixture of the Diels–Alder adduct (10b) and the azulene (9b) is formed.

Also, if (6f) is reacted with (8) in the much lower boiling benzene, the Diels–Alder adduct (10b) rather than the azulene (9b) is formed. No evidence was found for the formation of tricarbonyl(benzene)chromium. In the absence of (8), only decomposition of the heptafulvene complex results. This is surprising in view of the ready displacement of cycloheptatriene from tricarbonyl-(cycloheptatriene)chromium under similar conditions.[5]

Heptafulvene Complexes of Molybdenum and Tungsten.—The synthesis involved the use of the $(py)_3M(CO)_3$ (M = Mo or W) derivatives, following the method used by Pauson *et al.* in the preparation of tricarbonyl-(cycloheptatriene)chromium compounds.[10] Thus, reaction of the ligands (3a—c) with $(py)_3M(CO)_3$ gave the complexes (11a,b) and (12a—c). Reaction with Ph_3CX gave the tropylium salts (13a,b) and (14a—c) (see Table 1), and deprotonation with 1,8-bis(dimethylamino)-naphthalene gave the heptafulvene complexes (15a,b) and (16a,c) (see Table 2).

These compounds are less stable than the chromium compounds and have not been isolated. However, good

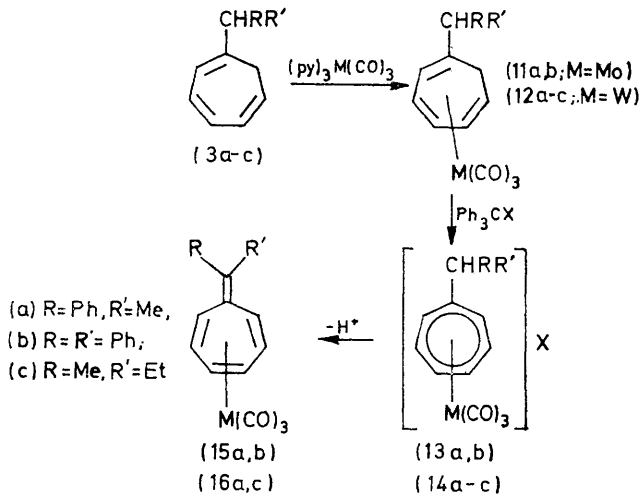


spectroscopic data have been obtained for some of the compounds *in situ*.

The molybdenum complexes readily undergo dissociation. Thus attempted sublimation of (15a) at 80° onto a cooled probe results in isolation of free 8-phenyl-8-methylheptafulvene (17) as an unstable red oil [n.m.r. (CS_2), Ph, τ 2·90, m, 5H; olefinic protons, τ 4·18, m, 6H; Me, τ 8·08, s, 3H, *m/e* 194].

[8] M. A. Haas, *Organometallic Chem. Rev.*, 1969, **4A**, 307.
[9] J. E. Mahler, D. A. K. Jones, and R. Pettit, *J. Amer. Chem. Soc.*, 1964, **86**, 3589.
[10] P. L. Pauson, G. H. Smith, and J. H. Valentine, *J. Chem. Soc.* (*C*), 1967, 1061.

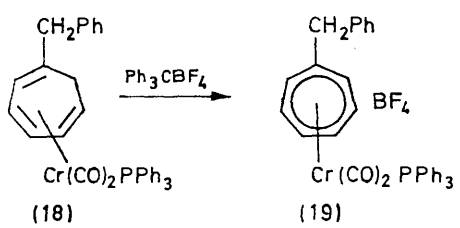
The tungsten complexes are even less stable, and cannot be purified sufficiently to obtain satisfactory n.m.r. spectra. A study of their reactivity has not been undertaken in view of their instability and, particularly



in the case of the tungsten complexes, the low yields obtained in several of the synthetic steps.

Phosphine Substituted Complexes.—In an attempt to stabilize the monosubstituted complexes (6e—g) by a change in the auxiliary ligands, the monophosphine substituted tropylium salt (19) was prepared by u.v. irradiation of (4f) in the presence of PPh_3, using the method of Anderson *et al.*,[11] to give (18) followed by hydride abstraction with Ph_3CBF_4 (see Table 1).

Complex (19) was found not to react with 1,8-bis-(dimethylamino)naphthalene. This decrease in the acidity of the exocyclic hydrogen is in accord with the greater σ-donor capability of the phosphine, and represents a marked change in reactivity from the tricarbonyl analogue. Attempted deprotonation with nucleophilic bases leads only to decomposition.



EXPERIMENTAL

N.m.r. spectra were recorded on a Varian HA100 spectrometer, i.r. spectra on a Perkin-Elmer 257, and mass spectra on an A.E.I. MS 9.

Microanalyses were performed by the University Chemical Laboratory Microanalytical Department.

$C_7H_7BF_4$,[12] Ph_3CSbF_6,[13] Ph_3CBF_4,[14] 7-ethoxy-,[15] methyl-,[16] and isopropyl-cycloheptatriene [16] were prepared by literature methods. 7-Ethylcycloheptatriene [17] was prepared by the method used for the isopropyl derivative.

[11] W. P. Anderson, W. G. Blenderman, and K. A. Drews, *J. Organometallic Chem.*, 1972, **42**, 139.
[12] K. Conrow, *Org. Synth.*, 1963, **43**, 101.
[13] D. W. A. Sharp and N. Sheppard, *J. Chem. Soc.*, 1957, 674.

7-(*Diphenylmethyl*)*cyclohepta*-1,3,5-*triene* (2b).—Butyllithium (15%, 30·2 ml, 82 mmol) in hexane was added to diphenylmethane (14·1 g, 82 mmol) in dry ether (170 ml) and refluxed for 18 h. The red solution of diphenylmethyllithium was transferred to a dropping funnel and added to a stirred suspension of tropylium tetrafluoroborate (14·6 g, 82 mmol) in ether (75 ml) at 0°. After warming to room temperature and stirring for 1 h the solution was filtered and the ether evaporated. Unreacted diphenylmethane was removed by vacuum distillation, and the residue was recrystallized from CCl_4 to give (2b) (11·4 g, 54%) as white crystals, m.p. 76—78° (Found: C, 93·0; H, 7·0. Calc. for $C_{20}H_{18}$: C, 93·3; H, 6·9%). N.m.r. (CCl_4) τ 4·90, m, $H^{1,6}$; τ 3·93, m, $H^{2,5}$; τ 3·38, m, $H^{3,4}$; τ 7·62, quint, H^7; τ 5·88, d, CH, *J* 6·2 Hz; τ 2·84, m, Ph.

7-*Benzylcyclohepta*-1,3,5-*triene* (2f).—Benzylmagnesium bromide was prepared by addition of benzyl bromide (36·4 g, 220 mmol) in dry ether (50 ml) to a stirred suspension of magnesium (5·20 g, 220 mmol) in ether (175 ml). To this was added 7-ethoxycycloheptatriene (17·0 g, 125 mmol) in ether (25 ml) at a rate sufficient to cause gentle reflux. This was stirred for 1 h and then hydrolysed with NH_4Cl solution (50 ml). The ether layer was washed with dilute HCl, water, and dried over $MgSO_4$. The ether was removed and the residue vacuum distilled to give compound (2f) (14·0 g, 64%), b.p. 84—88°, 0·1 mmHg (Found: C, 92·1; H, 7·5. Calc. for $C_{14}H_{14}$: C, 92·3; H, 7·7%). N.m.r. (CCl_4) τ 4·81, m, $H^{1,6}$; τ 3·90, m, $H^{2,5}$; τ 3·42, m, $H^{3,4}$; τ 8·02, quint, H^7; τ 7·08, d, CH_2, *J* 6·3 Hz; τ 2·84, m, Ph.

7-*s*-*Butylcyclohepta*-1,3,5-*triene* (2c).—sec-Butylmagnesium bromide was prepared by the addition of sec-butylbromide (18·4 g, 140 mmol) in ether to a stirred suspension of magnesium (3·4 g, 140 mmol) in ether (200 ml). 7-Ethoxycycloheptatriene (18·4 g, 140 mmol) in ether (30 ml) was added and the procedure followed as for compound (2f). Vacuum distillation gave (2c) (12·0 g, 58%); b.p. 52—54°, 10 mmHg (Found: C, 88·0; H, 11·7. Calc. for $C_{11}H_{16}$: C, 88·4; H, 11·6%). N.m.r. (CCl_4) τ 4·72, m, $H^{1,6}$; τ 3·85, m, $H^{2,5}$; τ 3·40, m, $H^{3,4}$; τ 8·08—8·26, m, H^7, CH, CH_2; τ 8·88—9·28, m, $2CH_3$.

7-(α-*Phenylethyl*)*cyclohepta*-1,3,5-*triene* (2a).—This was prepared by the entrainment method. Magnesium (11 g, 453 mmol) was suspended in ether (50 ml) and ethyl bromide (1 ml) added. When the ether had started to reflux, a solution of (α-chloroethyl)benzene (10 g, 70 mmol) and ethyl bromide (15 g, 140 mmol) in ether (150 ml) was added at a rate sufficient to cause gentle reflux. After addition was completed the solution was refluxed for ½ h, and 7-ethoxycycloheptatriene (19 g, 140 mmol) in ether (50 ml) was added with cooling. After refluxing for 45 min, the solution was cooled and hydrolysed with dilute HCl (50 ml). The ether layer was washed with water (3 × 100 ml) and dried over $MgSO_4$. Removal of the ether and vacuum distillation gave (2a) (11·0 g, 40%), b.p. 85—86°, 0·1 mmHg (Found: C, 91·2; H, 8·3. Calc. for $C_{15}H_{16}$: C, 91·8; H, 8·2%). N.m.r. (CCl_4) τ 4·94, m, $H^{1,6}$; τ 3·96, m, $H^{2,5}$; τ 3·46, m, $H^{3,4}$; τ 8·35, m, H^7; τ 7·09, m, CH; τ 2·99, m, Ph; τ 8·66, d, *J* 6·7 Hz, CH_3. Some 7-ethylcycloheptatriene (2e) was also obtained.

[14] H. J. Dauben, L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, 1960, **25**, 1442.
[15] T. Nozoe and K. Takahashi, *Bull. Chem. Soc. Japan*, 1965, **38**, 665.
[16] T. Nozoe, K. Takahashi, and H. Yamamoto, *Bull. Chem. Soc. Japan*, 1969, **42**, 3277.
[17] K. Conrow, *J. Amer. Chem. Soc.*, 1961, **83**, 2343.

1-*Isopropylcyclohepta*-1,3,5-*triene* (3d).—7-Isopropylcyclohepta-1,3,5-triene (10 g) dissolved in benzene (10 ml) and sealed under vacuum in a Carius tube was heated at 180° for 8 h. The residue was vacuum distilled, b.p. 48—54°, 20 mmHg, to give 8·5 g of an isomeric mixture consisting of predominantly the 1-isomer (3d). The same procedure was used for the other ligands.

Tricarbonyl(isopropyltropylium)chromium Tetrafluoroborate (5d).—Hexacarbonylchromium (5·0 g, 23 mmol) was heated under reflux in acetonitrile (50 ml) for 24 h.[18] The solvent was removed *in vacuo* and 3·1 g (23 mmol) of isomerized isopropylcycloheptatriene (3d) (3·1 g, 23 mmol) in dry tetrahydrofuran (75 ml) was added. The solution was refluxed for 4 h, after which it was filtered and the solvent removed. The residue was chromatographed on silica gel using ethyl acetate–light petroleum (1 : 10, b.p. 30—40 °C) to give tricarbonyl(isopropylcycloheptatriene)-chromium (4d) (3·80 g, 67%) as a red oil.

This was dissolved in dichloromethane (10 ml) and trityl tetrafluoroborate (4·65 g, 14 mmol) in dichloromethane (20 ml) was added. After stirring for 15 min the orange-brown solution was poured into dry ether (200 ml). The precipitate was collected and washed with ether to give (5d) (4·1 g, 82%) as an orange powder. The remaining tricarbonyl(tropylium)chromium salts were prepared in a similar fashion. In the case of (4a), Ph_3CSbF_6 was used to obtain a crystalline derivative [(5a) Found: C, 38·9; H, 2·9. Calc. for $C_{18}H_{15}CrF_6O_3Sb$: C, 38·2; H, 2·7. (5b) Found: C, 58·5; H, 4·2. Calc. for $C_{23}H_{18}BCrF_4O_3$: C, 57·5; H, 3·6. (5c) Found: C, 45·2; H, 4·0. Calc. for $C_{14}H_{15}BCrF_4O_3$: C, 45·4; H, 4·1. (5d) Found: C, 43·4; H, 3·8. Calc. for $C_{13}H_{13}BCrF_4O_3$: C, 43·8; H, 3·7. (5e) Found: C, 42·6; H, 3·5. Calc. for $C_{12}H_{11}BCrF_4O_3$: C, 42·2; H, 3·2. (5f) Found: C, 50·9; H, 3·5. Calc. for $C_{17}H_{13}BCrF_4O_3$: C, 50·5; H, 3·2%]. Tricarbonyl(methyltropylium)chromium perchlorate has been prepared previously.[5]

Tricarbonyl(8,8-dimethylheptafulvene)chromium (6d).—Compound (5d) (750 mg, 2·1 mmol) was suspended in chloroform (20 ml), and 1,8-bis(dimethylamino)naphthalene (450 mg, 2·1 mmol) in $CHCl_3$ (20 ml) was added dropwise over 10 min. After stirring for 15 min, the solution was filtered and the $CHCl_3$ removed. The residue was chromatographed on silica gel using ethyl acetate–light petroleum (1 : 20, b.p. 30—40 °C) to yield (6d) (360 mg, 64%). It was further purified by sublimation at 60°, 0·01 mmHg, to give a deep red oil which crystallized on the cold finger. The other disubstituted complexes were prepared in a similar manner; (6c) was purified by sublimation at 60°, 0·01 mmHg, while (6a,b) were crystallized from pentane. [(6a) Found: C, 66·2; H, 4·6. Calc. for $C_{18}H_{14}CrO_3$: C, 65·5; H, 4·3. (6b) Found: C, 70·8; H, 4·3. Calc. for $C_{23}H_{16}CrO_3$: C, 70·5; H, 4·1. (6c) Found: C, 60·3; H, 5·1. Calc. for $C_{14}H_{14}CrO_3$: C, 59·7; H, 5·0. (6d) Found: C, 58·7; H, 4·7. Calc. for $C_{13}H_{12}CrO_3$: C, 58·2; H, 4·5%]. The complexes (6e—g) decomposed on attempted purification and therefore the crude product obtained after the removal of the $CHCl_3$ was used for further reactions.

Tricarbonyl(isopropyltropylium)chromium Hexafluorophosphate (5d; X = PF_6).—Compound (6d) (100 mg, 36 mmol) was dissolved in ether (10 ml) and a few drops of 65% HPF_6 were added. The light orange precipitate of (5d; X = PF_6^-) (120 mg, 81%) was collected and washed with ether. The i.r. and n.m.r. spectra were identical to those of the tetrafluoroborate salt.

Similar behaviour was observed for the complexes (6b,g).

1-*Phenyl*-2,3-*methoxycarbonylazulene* (9b).—Tricarbonyl-(8-phenylheptafulvene)chromium (6f), prepared from (5f) (1·0 g) and 1,8-bis(dimethylamino)naphthalene (0·5 g) was dissolved in xylene (25 ml) containing dimethylacetylenedicarboxylic ester (8) (1·5 g). The solution was refluxed for 8 h and then the solvent was removed. The residue was chromatographed on alumina using ethyl acetate–benzene (1 : 20). Removal of the solvent from the purple band collected gave a purple oil, which was further purified by t.l.c. on silica gel using ethyl acetate–benzene (1 : 10) to give compound (9b) (100 mg, 13%).

Reaction of the heptafulvene complexes (6e,g) in the same manner gave the azulenes (9a,c). If the disubstituted complex (6d) is used, then the Diels–Alder adduct (10a) is obtained.

If the above reaction with (6f) is performed in refluxing nonane for 4 h, then a mixture of the azulene (9b) and the Diels–Alder adduct (10b) is obtained. In refluxing benzene after 8 h, the product is solely the Diels–Alder adduct (10b), with only a trace of the azulene.

TABLE 3

Azulene and Diels–Alder adducts

	P^+ (*m/e*)		
	Calc.	Found	U.v. (nm) [a]
(9a)	258·0891	258·0898	604, 591, 529, 304, 284, 237, 224
(9b)	320·1047	320·1054	595, 561, 518, 303, 274, 237, 234
(9c)	244·0735	244·0733	[b]
(10a)	274·1204	274·1199	
(10b)	322·1205	322·1212	

[a] Pentane solution. [b] Identical to that quoted by W. von E. Doering and D. W. Wiley, *Tetrahedron*, 1960, **11**, 183.

Tricarbonyl(α-phenylethyltropylium)molybdenum Hexafluoroantimonate (13a).—Hexacarbonylmolybdenum (3·8 g, 14·4 mmol) was refluxed in pyridine (25 ml) for 4 h. Removal of the pyridine gave yellow $(py)_3Mo(CO)_3$.[19] Isomerized α-phenylethylcycloheptatriene (3a) (2·1 g, 10·7 mmol) in ether (75 ml) was added, followed by freshly distilled BF_3,Et_2O (5·4 ml, 43·5 mmol). The suspension was refluxed with stirring for 1 h. The red solution was filtered, washed with water (3 × 100 ml), and dried over $MgSO_4$. Removal of the solvent and chromatography of the residue on silica gel using ethyl acetate–light petroleum (1 : 10, b.p. 30—40 °C) gave tricarbonyl(α-phenylethylcycloheptatriene)molybdenum (11a) (3·16 g, 63%).

This was dissolved in CH_2Cl_2 (10 ml) and Ph_3CSbF_6 (3·8 g, 7·95 mmol) in CH_2Cl_2 (20 ml) was added. After stirring for 10 min, the solution was poured into dry diethyl ether. The precipitate of (13a) (4·1 g, 85%) was collected and washed with ether (Found: C, 36·0; H, 2·5. Calc. for $C_{18}H_{15}F_6O_3MoSb$: C, 35·4; H, 2·5%).

Compound (13b) was prepared in a similar manner using Ph_3CBF_4 (Found: C, 52·9; H, 3·7. Calc. for $C_{23}H_{16}BF_4MoO_3$: C, 52·7; H, 3·3%).

Tricarbonyl(α-phenylethyltropylium)tungsten Hexafluoroantimonate (14a).—Hexacarbonyltungsten (7·0 g, 20 mmol) was heated under reflux in pyridine (30 ml) for 10 h and then the pyridine was removed to give orange $(py)_3W(CO)_3$.[20]

[18] D. P. Tate and W. R. Knipple, *Inorg. Chem.*, 1962, **1**, 433.
[19] W. Hieber and F. Muhlbauer, *Z. anorg. Chem.*, 1935, **221**, 337.
[20] W. Hieber and E. Romberg, *Z. anorg. Chem.*, 1935, **221**, 349.

1-(α-Phenylethyl)cycloheptatriene (3a) (2·5 g, 14 mmol) in Et_2O (75 ml) was added, followed by freshly distilled BF_3,Et_2O (7·5 ml, 60 mmol). The resulting suspension was refluxed for 4 h. The red solution was filtered, washed with water (3 × 100 ml), and dried with $MgSO_4$. Removal of solvent and chromatography of the residue on silica gel using ethyl acetate–light petroleum (1 : 10, b.p. 30—40 °C) gave tricarbonyl[1-(α-phenylethyl)cycloheptatriene]tungsten (12a) (1·35 g, 21%) as a red oil. This was dissolved in CH_2Cl_2 (10 ml) and Ph_3CSbF_6 (1·4 g, 2·92 mmol) in CH_2Cl_2 (15 ml) added. After 5 min stirring the solution was poured into ether (200 ml). The light red precipitate of (14a) (1·7 g, 84%) was collected and washed with ether (Found: C, 30·9; H, 2·2. Calc. for $C_{18}H_{15}F_6O_3SbW$: C, 30·8; H, 2·2%).

The salts (14b,c) were prepared similarly using Ph_3CBF_4 [(14b) Found: C, 44·9; H, 3·0. Calc. for $C_{23}H_{16}BF_4O_3W$: C, 45·2; H, 2·8. (14c) Found: C, 33·7; H, 3·3. Calc. for $C_{14}H_{15}BF_4O_3W$: C, 33·5; H, 3·0%).

Tricarbonyl(8-phenyl-8-methylheptafulvene)molybdenum (15a).—Compound (13a) (1·5 g, 2·46 mmol) was suspended in chloroform (20 ml), and 1,8-bis(dimethylamino)naphthalene (0·53 g, 2·46 mmol) added dropwise over 10 min. The solution was filtered and the solvent removed. Chromatography of the residue on silica gel using ethyl acetate–light petroleum (1 : 20, b.p. 30—40 °C) gave (15a) (300 mg, 32%) as a red oil. Attempted purification by sublimation resulted only in the liberation of free 8-phenyl-8-methylheptafulvene (17). Complexes (15b) and (16a,c) were prepared in a similar manner. The salt (14b) decomposed on treatment with 1,8-bis(dimethylamino)naphthalene.

Dicarbonyltriphenylphosphine(benzyltropylium)chromium Tetrafluoroborate (19).—Tricarbonyl(1-benzylcycloheptatriene)chromium (4f) (4·3 g, 13·5 mmol) was dissolved in tetrahydrofuran (100 ml) and cooled to −78°. Triphenylphosphine (4 g, 15·3 mmol) was added and the stirred solution irradiated with a long wavelength mercury lamp for 29 h. After filtration, the solvent was removed and the residue chromatographed on silica gel using benzene–light petroleum (30%, b.p. 30—40 °C). After elution of unchanged (4f) a brown-red band was collected, giving dicarbonyl(triphenylphosphine)(1-benzylcycloheptatriene)-chromium (18) (1·40 g, 20%) as brown-red crystals.

This was dissolved in CH_2Cl_2 (10 ml) and Ph_3CBF_4 (0·75 g, 2·27 mmol) in CH_2Cl_2 (10 ml) was added. After stirring for 10 min, the solution was poured into diethyl ether (150 ml). The light green precipitate of compound (19) (1·3 g, 90%) was collected and washed with Et_2O (Found: C, 64·5; H, 4·8. Calc. for $C_{34}H_{28}BCrF_4O_2P$: C, 64·2; H, 4·4%).

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