387. *Transition-metal Complexes of Seven-membered Ring Systems. Part IV.*[1] *Proton Resonance Spectra of Cycloheptatriene Complexes of Group VI Metals.*

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The tricarbonylmolybdenum derivatives of 1,1,4-trimethylcycloheptatriene and 1,1,3,4-tetramethylcycloheptatriene have been prepared. The comparison of high-resolution nuclear magnetic resonance spectra of these compounds and of the unsubstituted compound enables assignments of the spectra to be made.

By using *X*-ray data for the unmethylated complex $C_7H_8Mo(CO)_3$ and a much simplified model, an attempt is made to predict qualitatively the relative line positions for the complex.

The preparation and spectra of Group VI metal complexes of norbornadiene, bicyclo[2,2,2]octa-2,5-diene, and cyclo-octatetraene are given.

IN Part I [2] the preparation of tricarbonyl complexes of chromium and molybdenum with cycloheptatriene and some 1-substituted cycloheptatrienes was described. The high-resolution nuclear magnetic resonance spectra of these cycloheptatriene derivatives were very complex and could not be assigned at the time. Subsequent experience with the spectra of some conjugated diene–metal [1,3] and azulene [4] complexes, together with present measurements on molybdenum tricarbonyl derivatives of 1,1,4-trimethyl- and 1,1,3,4-tetramethyl-cycloheptatriene have enabled definite assignments of the spectral lines to be made.

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[1] Part III, Burton, Pratt, and Wilkinson, *J.*, 1961, 594.
[2] Abel, Bennett, Burton, and Wilkinson, *J.*, 1958, 4559.
[3] Green, Pratt, and Wilkinson, *J.*, (a) 1959, 3753; (b) 1960, 989.
[4] Burton, Pratt, and Wilkinson, *J.*, 1960, 4290.

(1) *Nuclear Magnetic Resonance Spectra of Cycloheptatriene Complexes.*—The high-resolution spectra of the parent olefins and of their complexes are given in detail in the Experimental section and are shown, approximately, in the Figure; chemical shifts are given in τ-values.

The spectra of the olefin–metal complexes are quite different from those of the parent hydrocarbons (cf. also refs. 1 and 3). In the parent trienes, there are three types of olefinic proton which give lines occurring at low fields although they are not completely equivalent. The two protons or methyl groups at position 1 are equivalent, probably as a result of a rapid averaging of conformational isomers.

On co-ordination to the metal atom, the changes in the spectra of the three types of olefinic proton present in the hydrocarbons are similar whether the metal atom is chromium, molybdenum, or tungsten. Thus the $\gamma(H_{4,5})$ protons shift upfield slightly (*ca.* 0·2—0·5 p.p.m.) and lie at *ca.* 4·0. The $\beta(H_{3,6})$ protons shift upfield by about 1·5 p.p.m. and lie at *ca.* 5·2, while the $\alpha(H_{2,7})$ protons shift by about 2·5 p.p.m. and lie at *ca.* 6·5. The two methylene protons are also now not equivalent. For the cycloheptatrienechromium complex $C_7H_8Cr(CO)_3$ they differ by *ca.* 1·6 p.p.m.; one is at a higher field than in the cycloheptatriene spectrum and the other, which lies at a lower field than in the cycloheptatriene spectrum, overlaps the lines of the α-protons. For $C_7H_8Mo(CO)_3$, the separation between the methylene group proton lines is smaller (*ca.* 1·0 p.p.m.) than for the chromium compound and both lie at lower fields than for cycloheptatriene. In the $C_7H_8W(CO)_3$ spectrum, both of the methylene proton lines overlap the α-proton lines and the separation between them appears to be small, but the spectrum of this compound was not well resolved, perhaps owing to traces of paramagnetic material produced by decomposition in the solvent used. The same trouble was encountered, though to a smaller extent, with the chromium and molybdenum compounds, whose spectra were slightly broadened. The methyl-substituted cycloheptatrienemolybdenum complexes, which are much more stable than the unsubstituted compound and are less sensitive to air when dissolved, gave sharp spectra. In the methylcycloheptatriene complexes the 1-methyl groups, like the protons of the methylene group in, say, $C_7H_8Cr(CO)_3$, are not equivalent, one methyl line moving upfield and one downfield to give a separation of more than 1 p.p.m. The methyl groups in the 3- and 4-positions move to lower fields in the spectrum of the metal complex, as compared with that of the hydrocarbon.

(2) *Qualitative Estimation of Chemical Shifts.*—It has proved possible to assign in a fairly unequivocal manner the resonance lines in the spectra of various olefin–metal complexes [1,3,4] and we have similarly assigned here the lines for the Group VI metal–cycloheptatriene complexes; also it has been shown that some olefinic protons in a bound conjugated olefin have resonances (due to terminal protons in a conjugated diene system) shifted to higher fields than others. However, it has not been possible, in the absence of accurate *X*-ray crystallographic data, to attempt to correlate the observed chemical shifts with any changes in the bond distances or angles in the hydrocarbon produced by co-ordination to the metal atom. The first *X*-ray crystallographic data on a conjugated olefin–metal complex, $C_7H_8Mo(CO)_3$, are now available, and we have attempted an interpretation of the chemical shifts.

In the structure of cycloheptatrienemolybdenum tricarbonyl [5] the metal atom is on one side of, and almost equidistant (*ca.* 2·35 Å) from, the six olefinic carbon atoms (C_2—C_7) which are virtually planar. The methylene group is bent out of this plane away from the metal atom and the three carbon monoxide groups are approximately diametrically opposite the positions of the double bonds. The C–C distances in the complex are about the same as those found in unco-ordinated conjugated olefins and show alternation corresponding to " double " and " single " bonds; the former are *ca.* 1·36 Å and the latter *ca.* 1·43 Å, while the C–C bonds to the methylene group are *ca.* 1·53 Å.

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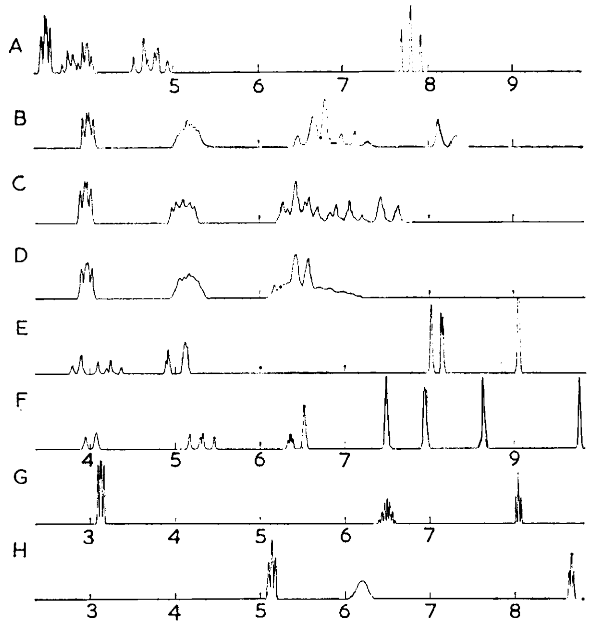
[5] Dunitz and Pauling, *Helv. Chim. Acta*, 1960, **43**, 2188.

The structure is thus consistent with the presence in the complex of three localised metal–olefin bonds formed by donation of an electron pair from each π-bond in the ring, presumably along the lines suggested for ethylene complexes.[6] There is no indication that σ-bonds are formed between the hydrocarbon and the metal atom, a conclusion in accord with the infrared spectra of the conjugated diene–metal complexes.[1,3,4] The shift of some of the olefinic proton resonances into the high-field region (where aliphatic proton resonances are found) in the conjugated diene– and triene–metal complexes cannot be attributed to the formation of σ-bonds to the metal atom, but can, we believe, now be qualitatively explained, although as yet in a very crude manner (owing to the lack of adequate data and the assumptions necessarily involved) by changes in the " long-range shielding " effects of π-electrons.

The resonance position of a proton in an olefin group depends partly on the diamagnetic shielding by the electrons of the C–H σ-bond. This shielding will alter with changes in the electronegativity of the carbon atom as, for example, when the π-electrons of a double bond are utilized in bonding to a transition-metal atom. However, the change should affect all the olefinic protons approximately equally, and it does not seem that this effect would be sufficient to account for the large separations observed in the metal complexes of conjugated olefins.

Proton resonance spectra (56·4 mc./sec.; *scale in τ values*; *magnetic field increases from left to right*).



A, Cycloheptatriene; B, cycloheptatriene-$Cr(CO)_3$; C, cycloheptatriene-$Mo(CO)_3$; D, cycloheptatriene-$W(CO)_3$; E, 1,1,3,4-tetramethylcycloheptatriene; F, 1,1,3,4-tetramethylcycloheptatriene-$Mo(CO)_3$; G, norbornadiene; H, norbornadiene-$Mo(CO)_4$.

An important contribution to olefinic proton shifts is the " long-range shielding " effect arising from the electrons in other bonds, notably the π-electrons.[7-10] The magnetic

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[6] Dewar, *Bull. Soc. chim. France*, 1951, **79**, 18.

[7] McConnell, *J. Chem. Phys.*, 1957, **27**, 226.

[8] Narashimhan and Rogers, *J. Phys. Chem.*, 1959, **63**, 1388.

[9] Jackman and Wiley, *J.*, 1960, 2881.

[10] Jackman, " Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959.

moment induced in the π-electrons by the applied magnetic field produces small additional magnetic fields at the protons, thereby altering their resonance positions. These small magnetic fields do not average to zero over all orientations because the diamagnetic susceptibility of π-electrons is anisotropic. The correct expression[8] for the shielding field is complicated and requires a knowledge of the three principal components of the susceptibility of the π-electrons, but a qualitative explanation of the long-range shielding effects in unco-ordinated olefins is obtained if the olefin group is represented by a point magnetic dipole. This dipole is placed at the electrical centre of the bond, *i.e.*, at the centre of the C–C σ-bond axis, and points in the direction of maximum magnetic susceptibility, *i.e.*, perpendicular to the plane of the C–H and C–C σ-bonds. The shielding field decreases with the inverse cube of the distance, away from the bond centre, and also varies with direction. The field is positive in regions above and below the plane of the olefin group inside solid cones extending from the point dipole symmetrically about its axis (for a diagram see ref. 10). Protons in these regions will experience an increased shielding producing a shift to higher fields. The field is negative in the region outside the cones and for a given distance is greater in the plane perpendicular to the dipole. The protons in a normal olefin lie in this plane and should experience a large negative shielding and this is believed to be the reason for the appearance of olefinic proton resonances in low-field regions of the spectrum.

The long-range shielding will certainly alter when π-electrons are involved in metal bonding. It is obvious that in a metal–olefin bond the electrical centre of this bond cannot be at the centre of the C=C bond as in the hydrocarbon but must be displaced towards the metal atom. Also, the direction of the maximum susceptibility of the bond depends on the directional relation of the metal to C=C axis; such changes would affect both the distance and orientation of the point dipole relative to the olefin protons. We can note here that in complexes of cyclic polyolefins and of such chelating dienes as norbornadiene, butadiene, etc., the conformation of the olefin will not allow the metal atom to occupy a position normal to the C=C bond axis as in ethylene complexes. In fact the line joining the metal atom to the centre of each double bond may not even be the line of maximum density.

We have attempted to represent the induced magnetic moment of the metal–olefin bond by a point magnetic dipole in order to calculate the long-range shielding effect on the co-ordinated olefinic protons. This procedure is obviously a vast oversimplification in view of the unknown factors.

In order to calculate the shielding effect on the protons in the complex it is necessary first to estimate where the proton resonances in the unco-ordinated cycloheptatriene skeleton fixed in the same configuration as in the complex would lie in the absence of any long-range shielding due to π-electrons. It is difficult to make this estimate, but it is clear that they would move upfield from the olefinic region and would probably lie close together. While the corrected position of the methylene protons would be *ca.* τ 8—8·5, the other protons could be grouped in the region 5·5—8. The shielding due to the π-contribution in the metal–olefin bonds is then superimposed. The π-contribution in the complex we take as being that due to three identical magnetic point dipoles located along the metal-to-double-bond axis. Each proton in the co-ordinated olefin experiences a contribution from each of the three dipoles, and in theory the algebraic sum of these contributions for each proton can be calculated with the dipoles in different orientations, the aim being to reproduce the observed resonance pattern. In the absence of a reliable estimate of the " skeletal " resonance positions, a variety of arrangements of the magnetic dipole of the metal–olefin bond are possible. However, the observed spectra of the complex being considered it seems likely that the algebraic sums of the three dipole contributions should give a net negative value for the γ-protons, a slight negative value for the β-protons, and a small negative or positive value for the α-protons. The methylene-protons should be different and have a negative contribution.

We have tried several arrangements and the type that best seems to reproduce the relative shifts is one where the magnetic point dipole points along the metal to C=C axis and is located at about one-third to one-quarter of the distance towards the metal atom. In this orientation, each olefin proton receives a small negative contribution from the dipole of its own metal–olefin bond but the contributions from the other two dipoles differ for the α-, β-, and γ-protons. The α-, β-, and γ-protons receive negative contributions from other two dipoles but their magnitudes decrease in the order $\alpha > \beta > \gamma$. Also, the two methylene-protons receive different negative contributions, the outer proton receiving the more negative. The magnitude of these field contributions depends on the magnetic moment of the point dipoles and we can use the observed separation between the two methylene-protons (*ca.* 1 p.p.m.) to convert the contributions to p.p.m. The addition of these contributions as p.p.m. to the above skeletal positions then reproduces fairly well the main features of the observed spectrum.

The relative shifts of the methyl groups in methyl-substituted cycloheptatriene complexes also seem to agree with this model; the estimated shifts are averaged over all orientations to allow for free rotation of the methyl groups.

The chromium and tungsten complexes have infrared and nuclear resonance spectra very similar to those of the molybdenum compound, and their structures are presumably similar. The nuclear magnetic resonance spectra differ mainly in the position for the methylene-protons. This is not unexpected, since small changes in the bond angles and distances in the metal–olefin group can produce larger changes in the orientation of the methylene group, thereby changing the field contribution at the two protons. The close similarity of the three groups of olefinic resonances in the chromium, molybdenum, and tungsten compounds suggests that the resonance positions are little dependent on the nature of the metal carbonyl part of the molecules.

(3) *Norbornadiene and Other Olefin–Metal Complexes.*—The proton resonance spectra of the norbornadiene complexes of molybdenum and chromium show three groups of lines similar to those from norbornadiene itself, indicating that the olefin has not isomerised in the complexes. Relative to their positions in spectra of the parent olefin, the methylene-protons occur at higher fields and the tertiary protons at slightly lower fields. The olefin-protons show larger shifts to higher fields although they are not so large as the shift found for the norbornadieneiron tricarbonyl complex.[3b] Although norbornadiene is unconjugated, it has a rigid structure which probably does not allow the olefin–metal axis to be perpendicular to the olefin groups, a situation similar to that of the cyclic olefin complexes. The observed shifts are compatible with a model involving two metal–olefin dipoles in orientations similar to those assumed for the cycloheptatriene complex.

The shifts in metal complexes of conjugated dienes [1,3] can also be explained qualitatively by similar models with two point dipoles. The type of structure usually accepted for these compounds is similar to that of the cycloheptatriene complex with the metal atom on one side of a planar olefin group. Again in this type of structure the metal–olefin axis is not perpendicular to the plane of the olefin group; rough calculations, with the dipole assumed along the metal to C=C bond about one-third towards the metal atom, predict a large separation between the central and the terminal protons of the diene system, as we have observed.

In the ethyleneplatinum compounds, on the other hand, the metal–olefin axis is perpendicular to the plane of the ethylene molecule. On our present model, the point dipole would point along this direction, as in ethylene itself. The four protons would experience the same shielding field and, if the electrical centre of the bond is not displaced too far towards the metal atom, the shielding field would still be negative and could be almost as great as in ethylene itself. It has been found that the proton resonance in ethylene-platinum complexes is little shifted from ethylene itself.[11]

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[11] Powell and Sheppard, *J.*, 1960, 2519.

We have also considered other models in which the dipole is oriented either perpendicular to the metal to C=C plane or parallel to the C=C axis. These orientations do not produce chemical shifts in the right directions, especially for methylene-protons in the cycloheptatriene complexes. The parallel, or at least some angular, orientation might be the most satisfactory if it is accepted, as has often been discussed that there is an appreciable amount of π-bonding between the metal atom and the olefin group owing to back-donation from the metal atom into anti-bonding π-orbitals on the carbon atoms. Whilst we have found that the orientation of the dipole along the metal to C=C axis is more satisfactory, this really gives no indication of the actual electron-density distribution in the metal–olefin bond.

We have not considered the contributions from other groups present in the molecules, such as the carbonyl groups, but these alone do not appear to produce sufficiently large effects to account for the olefinic shifts—for example, the olefinic resonances in the cyclopentadieneiron compounds are the same when the other groups present are so different as benzene,[3b] three carbonyls, or one triphenylphosphine and two carbonyl groups.[12]

EXPERIMENTAL

Microanalyses and molecular-weight determinations (ebullioscopic in benzene) were done by the Microanalytical Laboratory of this College.

Starting Materials.—1,1,3,4-Tetramethylcycloheptatriene was prepared by treating eucarvone [from (+)-carvone [13]] with methyl-lithium and dehydrating the resulting alcohol.[14] 1,1,4-Trimethylcycloheptatriene was obtained from Professor Alder's laboratory, Cologne. Cycloheptatriene and norbornadiene were generously presented by Shell Chemical Co., cyclooctatetraene by the British Oxygen Co., the bicyclo-octadiene by Professor Grob, Basle, and metal carbonyls by the Climax Molybdenum Co.

1,1,4,-*Trimethylcycloheptatrienemolybdenum Tricarbonyl.*—The olefin (2 g.) and excess of molybdenum carbonyl (5 g.) were heated in aromatic-free light petroleum (b. p. 100—120°) (40 ml.) under nitrogen for 7 hr. Removal of solvent and excess of carbonyl at 40°/1 mm. left red crystals (3·8 g.) which on sublimation at 90—100°/10^{-4} mm. gave the orange-red *complex*, m. p. 86—87° (80—90% yield) (Found: C, 49·8; H, 4·8; O, 15·5; Mo, 30·6%; *M*, 312. $C_{13}H_{14}MoO_3$ requires C, 49·7; H, 4·8; O, 15·3; Mo, 30·5%; *M*, 314).

1,1,3,4-*Tetramethylcycloheptatrienemolybdenum Tricarbonyl.*—This *complex* was prepared in a similar manner and sublimed at 120—130°/10^{-4} mm. as red crystals, m. p. 119—120° (yield 80—90%) (Found: C, 51·3; H, 5·0; O, 14·8; Mo, 29·4%; *M*, 324. $C_{14}H_{16}MoO_3$ requires C, 51·2; H, 4·9; O, 14·6; Mo, 29·2%; *M*, 328).

The two preceding compounds can also be purified by crystallisation from light petroleum (b. p. 30—40°) at −78°. These methyl-substituted compounds are more soluble in organic solvents and are both thermally, and, in polar solvents, oxidatively, more stable than the corresponding cycloheptatriene compound. Thus acetone solutions of the latter are decomposed by air within a few minutes, whereas the methyl-substituted compounds can be held in solution for several hours. This enhanced stability can be attributed to the electron-donor effect of the methyl groups which eases transfer of electron density from the olefin to the metal atom, and hence the bond strength.

Cycloheptatrienetungsten Tricarbonyl.—The hexacarbonyl (3 g.) and olefin (10 ml.) in 2,2′-dimethoxydiethyl ether (40 ml.) were heated at 190° in nitrogen for 6 hr. After evaporation at 80°/0·5 mm. the dark red oily residue was extracted with hot light petroleum (b. p. 60—80°; 3 × 15 ml.) and, after reduction to *ca.* 30 ml., the extract was cooled to −78°. The red crystals sublimed at 80—90°/10^{-4} mm. as needles, m. p. 117—118° (yield, 0·3 g.) (Found: C, 33·3; H, 2·3; O, 13·1%; *M*, 355. $C_{10}H_8O_3W$ requires C, 33·4; H, 2·2; O, 13·3%; *M*, 360). The tungsten *compound* is similar to the chromium and the molybdenum analogue [2] and appears to be intermediate between them in stability to air-, both in solution and in the solid state; the

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[12] Davison, Pratt, and Wilkinson, unpublished results.

[13] Corey and Burke, *J. Amer. Chem. Soc.*, 1956, **78**, 174.

[14] Corey, Burke, and Remers, *J. Amer. Chem. Soc.*, 1956, **78**, 180; Alder, Kaiser, and Schumacher, *Annalen*, 1957, **602**, 80.

compound has also recently been obtained by the reaction of cycloheptatriene with cyclo-octa-1,5-dienetungsten tetracarbonyl.[15]

Norbornadienechromium Tetracarbonyl.—The hexacarbonyl (5 g.) and olefin (8 ml.) were refluxed in aromatic-free light petroleum (b. p. 100—120°; 40 ml.) under nitrogen for 2 days. After evaporation at 50°/10^{-2} mm. sublimation gave the orange-yellow *tetracarbonyl*, m. p. 92—93° (yield, 1·7 g.) (Found: C, 51·8; H, 3·3; O, 24·7%; *M*, 251. $C_{11}H_8CrO_4$ requires C, 51·6; H, 3·1; O, 25·0%; *M*, 256).

Norbornadienemolybdenum Tetracarbonyl.—This was prepared as in the preceding case, except that the mixture was refluxed for only 20 hr. Removal of volatile material left a leathery polymer mixed with crystals; the latter were extracted with boiling light petroleum (b. p. 40—60°; 3 × 15 ml.), and the filtered extract was cooled to −78° to give pale yellow plates, m. p. 77—78° (yield, 60—70%) (Found: C, 44·0; H, 2·9; O, 21·3; Mo, 32·0%; *M*, 304. Calc. for $C_{11}H_8MoO_4$: C, 44·0; H, 2·7; O, 21·3; Mo, 32·0%; *M*, 300). This compound, which has previously been noted briefly,[16] sublimes in a vacuum below 80° but at higher temperature decomposes extensively.

The corresponding tungsten compound can be obtained in very low yield when the reagents are refluxed in 2,2′-dimethoxydiethyl ether; it was identified only by its infrared spectrum.

As in the cycloheptatriene series, the norbornadienechromium complex is more stable to air and more deeply coloured than the molybdenum complex. However, the latter is considerably more stable to air than cyclo-octa-1,5-dienemolybdenum tetracarbonyl, which confirms other evidence that norbornadiene is the most effective chelating diolefin so far investigated.

Bicyclo[2,2,3]*octa*-2,5-*diene*- (A) *and cyclo-octa*-1,5-*diene-molybdenum Tetracarbonyls* (B).[17]—These *compounds* were obtained by heating the hexacarbonyl (1 g.) and olefin (0·5 g.) in light petroleum (b. p. 100—120°; 30 ml.) under nitrogen for 20 hr. After removal of volatile matter the complexes crystallised from light petroleum (b. p. 40—60°) at −78° as yellow plates (A), m. p. 80° (decomp.) (Found: C, 45·6; H, 3·5; O, 20·6; Mo, 30·1%; *M*, 312. $C_{12}H_{10}MoO_4$ requires C, 45·8; H, 3·2; O, 20·4; Mo, 30·6%; *M*, 314), or cream needles (B), m. p. 119—120° (decomp.) (yield 40%) (Found: C, 45·3; H, 4·0; O, 20·4; Mo, 30·6%; *M*, 311. $C_{12}H_{12}MoO_4$ requires C, 45·6; H, 3·8; O, 20·2; Mo, 30·6%; *M*, 316).

Dicyclo-octatetraenemolybdenum Tetracarbonyl.—The hexacarbonyl (10 g.) and cyclo-octatetraene (5 ml.) were refluxed in light petroleum (b. p. 100—120°) for 20 hr. After evaporation of the red-brown solution at 50°/10^{-3} mm., the residue was extracted with hot benzene (3 × 20 ml.). After reduction to 15 ml., the extract was chromatographed on alumina with benzene as eluant. Two bands were obtained, the first of which gave pale yellow crystals (0·5 g.), from 1 : 1 benzene–light petroleum (b. p. 60—80°), of *dicyclo-octatetraenemolybdenum tetracarbonyl*, m. p. 190—192° (decomp.) (Found: C, 57·8; H, 4·3; O, 15·3; Mo, 23·3%; *M*, 419. $C_{20}H_{16}MoO_4$ requires C, 57·7; H, 3·9; O, 15·4; Mo, 23·0%; *M*, 416). The second band contained a rather air-sensitive substance, in low yield; this was not characterised. The first compound is insoluble in light petroleum but sublimed at *ca.* 180° in a vacuum. On catalytic hydrogenation of the complex (9·319 mg.) in ethyl acetate over Adams catalyst, 0·496 ml. (S.T.P.) of hydrogen was absorbed, corresponding to 1 mol. of hydrogen and indicating the presence of a double bond. It seems reasonable to conclude that this molybdenum tetracarbonyl complex has bound to it a cyclo-octatetraene dimer with three double bonds, only the two conjugated double bonds being utilized in bonding to the metal atom. However, since the dimer with three double bonds [18] does not appear to react with molybdenum carbonyl the co-ordinated olefin may have a different configuration; the nuclear magnetic resonance spectrum of the compound is very complicated and we have not as yet been able to interpret it.

Infrared Spectra.—Spectra were recorded on a Perkin–Elmer Model 21 instrument with sodium chloride and calcium fluoride optics and carbon disulphide, chloroform, and carbon tetrachloride in the appropriate regions. The spectra of the cycloheptatriene complexes are similar to that for $C_7H_8Mo(CO)_3$[2] except for additional bands for the methyl-substituted complexes; the norbornadiene complexes have spectra similar to those of other norbornadiene

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[15] Manuel and Stone, *Chem. and Ind.*, 1960, 231.

[16] Pettit, *J. Amer. Chem. Soc.*, 1959, **81**, 1266.

[17] Manuel and Stone, *Chem. and Ind.*, 1959, 1349; Bennett and Wilkinson, *ibid.*, 1959, 1516; Fischer and Frohlich, *Chem. Ber.*, 1959, **92**, 2995.

[18] Jones, *J.*, 1953, 2036.

complexes.[19] Norbornadienechromium tetracarbonyl shows four carbonyl bands, at 2033vs, 1959ms, 1944vs, and 1913vs cm.$^{-1}$, but for the molybdenum and tungsten compounds only three bands could be resolved.

Nuclear Magnetic Resonance Spectra and Assignments.—Proton resonance spectra were recorded at 56·4 Mc./sec. and 22° ± 1° on a Varian instrument. Carbon tetrachloride solutions were used and line positions are given in τ values (10·00 minus the position in p.p.m. on low-field side of tetramethylsilane as internal reference). Cycloheptatriene has been measured previously.[1]

1,1,4-*Trimethylcycloheptatriene.* 3·81, unsymmetrical doublet (6·2 c./sec.), H_5 split by H_6 (AB pair); 4·12, double doublet, H_6 split by H_5 (6·2 c./sec.) and H_7 ($\sim$9·0 c./sec.); 4·17, unsymmetrical doublet ($\sim$9·0 c./sec.), H_3 split by H_2 (AB pair); 5·07 and 5·04, H_2 and H_7 each split into an unsymmetrical doublet (AB pair) by H_2 and H_6 respectively; 8·01, single (width 3 c./sec.), 4-methyl group; 9·03, single (width 1 c./sec.), 1-methyl groups.

1,1,3,4-*Tetramethylcycloheptatriene.* 3·84, unsymmetrical doublet (6·2 c./sec.), H_5 split by H_6 (AB pair); 4·22, double doublet, H_6 split by H_5 (6·2 c./sec.) and by H_7 (9·6 c./sec.); 5·03, doublet (9·6 c./sec.), H_7 split by H_6; 5·16, *ca.* single, H_2 (overlaps one component of H_7); 8·03, singlet, 4-methyl group; 8·15, doublet (1·2 c./sec.), 3-methyl group split by H_2; 9·06, singlet, two 1-methyl groups.

Cycloheptatrienemolybdenum tricarbonyl. 3·95, double doublet (outer separation 7·6 c./sec., inner, $\sim$2 c./sec.), $H_4 + H_5$ split by each other and by H_3 and H_6; 5·11, $\geqslant$ five components, *ca.* 4 c./sec. separation, H_3 and H_6 split by H_2 and H_4 and by H_5 and H_7, respectively; *ca.* 6·5, double triplet (?), H_2 and H_7 split by H_3 and H_6, respectively, and by $>CH_2$ protons; *ca.* 6·9, complex, one $>CH_2$ proton; *ca.* 7·55, doublet (AB pair, 12 c./sec.), one proton of $>CH_2$ split by the other.

1,1,4-*Trimethylcycloheptatrienemolybdenum tricarbonyl.* 4·12, doublet (AB pair, 7·2 c./sec.), H_5 split by H_6; *ca.* complex, $H_6 + H_3$; 6·52, doublet (*ca.* 9·5 c./sec.), H_2 and H_7 split by H_3 and H_7, respectively; 7·48, single, 4-methyl group; 8·60, single, and 9·70, single, the 1-methyl groups.

1,1,3,4-*Tetramethylcycloheptatrienemolybdenum tricarbonyl.* 4·02, doublet (AB pair, 7·1 c./sec.), H_5 split by H_6; 5·31, double doublet, H_6 split by H_5 (7·1 c./sec.) and H_7 (*ca.* 9·0 c./sec.); 6·28, doublet and triplet (?), H_7 split by H_6 (8·6 c./sec.) and H_5; 6·44, single (width 2·3 c./sec.), H_2; 7·49, single, 4-methyl group; 7·94, doublet (splitting *ca.* 1·5 c./sec.), 3-methyl group; 8·63 and 9·77, both single, two 1-methyl groups.

Cycloheptatrienechromium tricarbonyl. 3·99, double doublet (7·6 c./sec. overall, 2 c./sec. inner separation), $H_4 + H_5$ split by each other and by H_3 and H_6; 5·17, complex, unresolved, H_3 plus H_6; *ca.* 6·6, H_3 and H_7, *ca.* 7·1, one of $>CH_2$ protons; 8·23, unsymmetrical doublet (*ca.* 12·6 c./sec.), one $>CH_2$ proton split by the other (AB pair).

Cycloheptatrienetungsten tricarbonyl. 3·96, double doublet (7·2 c./sec. overall, inner pair unresolved), H_4 and H_5; 5·18, complex but unresolved, H_3 and H_6; 6·1—7·2, overlapping bands of H_3, H_7 and both $>CH_2$ protons.

Norbornadiene. The spectrum has been given previously [3b] and a complete analysis of the spin-coupling interactions has also been given.[20]

Norbornadienechromium tetracarbonyl. 5·58, " triplet " (4·8 c./sec. overall) olefinic protons; 6·27, complex, unresolved, tertiary protons; 8·70, triplet (1·4 c./sec.), $>CH_2$ protons split by tertiary protons.

Norbornadienemolybdenum tetracarbonyl. 5·15, " triplet " (4·4 c./sec. overall), olefinic protons; 6·22 (no structure resolved; width *ca.* 8 c./sec.), tertiary protons; 8·67, triplet (1·3 c./sec.), $>CH_2$ protons split by tertiary protons.

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