

### 164. *Allyl, Alkyl, and Olefin Complexes of Molybdenum.*

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The preparation of the allyl complexes,  $C_5H_5Mo(CO)_3\sigma\text{-CH}_2\text{-CH=CH}_2$  and  $C_5H_5Mo(CO)_2\pi\text{-C}_3H_5$  is described. The  $\sigma$ -allyl complex reacts readily with hydrogen chloride forming the propene cation  $[C_5H_5Mo(CO)_3\text{-CH}_2\text{-CHMe}]^+$ . Reduction of the related ethylene cation fluoroborate,  $[C_5H_5Mo(CO)_3\text{-CH}_2\text{-CH}_2]^+\text{BF}_4^-$  by sodium borohydride affords the ethyl complex,  $C_5H_5Mo(CO)_3C_2H_5$ . The last reaction is shown to be reversible. Treatment of the  $\pi$ -allyl complex with hydrogen chloride in the presence of air affords a diamagnetic molybdenyl compound,  $C_5H_5MoO_2Cl$ .

The infrared and high-resolution nuclear magnetic resonance spectra of the compounds are given.

RECENTLY a number of allyl complexes of transition metals have been described.<sup>1</sup> After our studies of the cyclopentadienyl-iron-allyl system<sup>1</sup> we have now investigated the related complexes of molybdenum.

*Preparation and Chemical Properties.*—The compounds prepared in this work are given in Table I. The  $\sigma$ -allyl complex (I) is prepared in high yield by reaction of the sodium

TABLE I.

Compound	Form	M. p. or b. p.	-C≡O stretch †
$C_5H_5Mo(CO)_3\sigma\text{-CH}_2\text{-CH=CH}_2$ .....	Pale yellow oil	$\sim -5^\circ$ ( $60^\circ$ *)	2021vs, 1911vs, 1856vs
$C_5H_5Mo(CO)_2\pi\text{-C}_3H_5$ .....	Lemon-yellow crystals	$\sim 134$ *	1961vs, 1886s(sh), 1871vs
$[C_5H_5Mo(CO)_3\text{-CH}_2\text{-CH-CH}_3]^+\text{PF}_6^-$	Yellow powder	—	2110vs, 2062vs, 2008vs, 1980s(sh)
$[C_5H_5Mo(CO)_3\text{-CH}_2\text{-CH-CH}_2\text{D}]^+\text{PF}_6^-$	Yellow powder	—	2112vs, 2064vs, 2010vs, 1975s(sh)
$[C_5H_5Mo(CO)_3C_2H_4]^+\text{PF}_6^-$ .....	Yellow powder	—	2105vs, 2060vs, 2010vs
$C_5H_5MoO_2Cl$ .....	Pale yellow crystals	$\sim 140$ *	

\* Decomp. † For conditions of measurement see Experimental section.

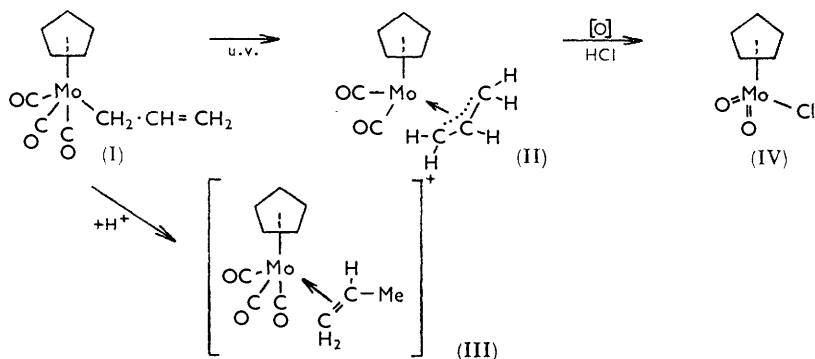
salt<sup>2</sup>  $Na^+[C_5H_5Mo(CO)_3]^-$  with an excess of allyl chloride. As for the  $\pi$ -allyl complex of iron,<sup>1</sup> the  $\pi$ -allyl derivative (II) could not be prepared readily by thermal decomposition of the  $\sigma$ -allyl complex (I). Heating the compound alone or in an inert solvent resulted mainly in the formation of the binuclear species  $[C_5H_5Mo(CO)_3]_2$ .<sup>2</sup> However, ultraviolet irradiation of the  $\sigma$ -allyl complex (I) *in vacuo* resulted in the formation of the  $\pi$ -complex (II) in considerably better yields. The compound (I) is a thermally unstable oil which is readily oxidized in air. The  $\pi$ -complex (II) is more stable and the sublimable yellow crystals remain unchanged in air for several days.

Light petroleum solutions of the  $\sigma$ -allyl complex (I) react with hydrogen chloride immediately, forming the propene cation (III) in high yields. The cation (III) chloride is readily soluble in water with which it reacts steadily, evolving a gas, and the neutral chloride<sup>2</sup>  $C_5H_5Mo(CO)_3Cl$  may then be isolated. If the aqueous solutions are treated immediately with solutions containing suitable large anions, then precipitates are obtained.

<sup>1</sup> Green and Nagy, *J.*, 1963, 189, and references therein.

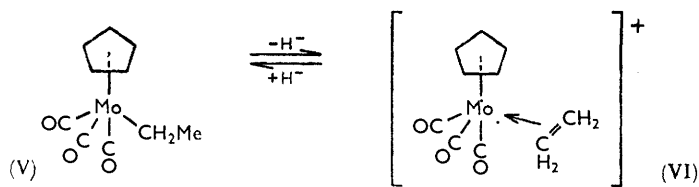
<sup>2</sup> Piper and Wilkinson, *J. Inorg. and Nuclear Chem.*, 1956, **3**, 104.

The hexafluorophosphate and hexachloroplatinate of cation (III) may be prepared in this way. The hexafluorophosphate is moderately stable in air and soluble in acetone, tetrahydrofuran, and liquid sulphur dioxide. It has been shown that the propene complex of iron does not exchange protons when dissolved in deuterium oxide.<sup>1,3</sup> Accordingly, the



complex (I) was treated with deuterium chloride, and the cation formed was extracted into water from which it was immediately precipitated as the hexafluorophosphate. The spectra of the deuterated cation are given below. The related ethylene cation (VI) may be prepared in good yields by abstraction of a hydride ion from the previously described ethyl complex<sup>2</sup> (V). Treating chloroform solutions of the latter with stoichiometric amounts of triphenylmethyl fluoroborate gives a yellow salt which the evidence shows to be the cation (VI) fluoroborate. This cation has also been prepared by reaction of ethylene with the complex  $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$ .<sup>4</sup> As distinct from the iron-alkyl complexes,<sup>5</sup> triphenylmethyl perchlorate was not a suitable reagent for hydride abstraction as it caused rapid decomposition of tetrahydrofuran solution of the ethyl compound (V).

Reduction, by sodium borohydride, of tetrahydrofuran solutions of the ethylene cation (VI) fluoroborate affords the ethyl complex (V) in moderate yields. Therefore, as for the related iron complexes,<sup>6</sup> the hydride abstraction is reversible.



*Infrared Spectra.*—The spectra are given in the experimental section, except for the C=O stretches which are given in Table 1. All spectra show peaks characteristic of a cyclopentadienyl group. The spectra of the complexes (I)—(III) are very similar to those of the analogous compounds of iron.<sup>1</sup> Here also, the C-H stretching region of the propene cation (III) is anomalous in that there is not the characteristic absorption of a methyl group. The spectrum of the deuterated cation differs from that of (III) in that peaks at 1462, 1407, 1382, and 1360  $\text{cm}^{-1}$  are less intense and new peaks appear at 1296 and 1275  $\text{cm}^{-1}$ . The former changes are in the region assignable to C-H bending vibrations. There are also slight differences in the spectra in the region 2800—3100  $\text{cm}^{-1}$ . The spectrum of the cation (VI) is the same, where comparable, with that previously reported.<sup>4</sup>

<sup>3</sup> Green and Nagy, *Proc. Chem. Soc.*, 1961, 378.

<sup>4</sup> Fischer and Fichtel, *Chem. Ber.*, 1961, **94**, 1200.

<sup>5</sup> Green and Nagy, *Proc. Chem. Soc.*, 1962, 74.

<sup>6</sup> Green and Nagy, *J. Amer. Chem. Soc.*, 1962, **84**, 1310.

*Proton Magnetic Resonance Spectra.*—The peaks are given in Table 2, with some assignments. The spectra of the complexes (I)—(III) are very similar to those of the related iron complexes<sup>1</sup> and are consistent with the formulations given. For the allyl complex (II), the band at 9.18  $\tau$ , assigned to the H<sup>3</sup> protons (see Table 2), is very broad although all other lines in the spectra are sharp. This effect was observed for both benzene and carbon disulphide solutions.

The spectrum of the deuterated cation shows that the doublet assigned to the methyl group of the undeuterated complex (III) has become a complex band of approximate intensity two. This band is therefore assigned to a CH<sub>2</sub>D group.

Both the proton magnetic resonance and the infrared spectra of the deuterated cation indicate that there is a small amount of impurity of the protonated isomer.

*Reaction of the  $\pi$ -Allyl Complex (II) with Hydrogen Chloride.*—The reaction of the complex (II) with hydrogen chloride might have been expected to yield an ethylenic species such as C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>2</sub>(CH<sub>2</sub>=CHMe)Cl which would be isoelectronic with the known tricarbonyl compound C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>Cl.<sup>2</sup> Infrared evidence shows that the products contain

TABLE 2.  
Nuclear magnetic resonance data.

Compound	Band pos. ( $\tau$ )*	Rel. intensity †	Multiplicity	Seprn. of components (c./sec.) ‡	Assignment
(C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> $\sigma$ -C <sub>3</sub> H <sub>5</sub> as pure liq.) 	7.73	2	2	app. <i>J</i> (CH <sub>2</sub> , 2) 8.0	CH <sub>2</sub> split by H-
	Centre, 6.5	2	Complex band (8)	—	H <sup>3</sup> and H <sup>4</sup>
	4.89	5	1	—	$\pi$ -C <sub>5</sub> H <sub>5</sub>
C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>2</sub> $\pi$ -C <sub>3</sub> H <sub>5</sub> in C <sub>6</sub> H <sub>6</sub> & CS <sub>2</sub> 	9.13	2	Broad doublet, peaks at 9.08, 9.28	—	H <sup>3</sup> protons split by H <sup>1</sup>
	7.40	2	4	app. <i>J</i> (2, 1) 7.6	H <sup>2</sup> split by H <sup>1</sup> and H <sup>3</sup>
	6.72	1	Complex band (4)	app. <i>J</i> (2, 3) 1	H <sup>1</sup>
[C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> C <sub>3</sub> H <sub>8</sub> ] <sup>+</sup> PF <sub>6</sub> <sup>-</sup> in liq. SO <sub>2</sub> 	7.99	3	2	app. <i>J</i> (CH <sub>3</sub> , 2) 6.8	CH <sub>3</sub> split by H <sup>2</sup>
	6.44	2	3	app. <i>J</i> (2, 3) 8.0	H <sup>3</sup> and H <sup>4</sup> split by H <sup>2</sup>
	Centre 4.98	1	Complex band (7)	---	H <sup>2</sup>
[C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> C <sub>3</sub> H <sub>5</sub> D] <sup>+</sup> PF <sub>6</sub> <sup>-</sup> in liq. SO <sub>2</sub> 	7.97	2	Complex band (6)	—	CH <sub>2</sub> D
	6.44	2	3	app. <i>J</i> (2, 3) 8.0	H <sup>3</sup> and H <sup>4</sup> split by H <sup>2</sup>
	4.72	1	Complex band (6)	app. <i>J</i> (2, 4) 16.0	H <sup>2</sup>
C <sub>5</sub> H <sub>5</sub> MoO <sub>2</sub> Cl in CS <sub>2</sub> 	4.05	5	1	—	$\pi$ -C <sub>5</sub> H <sub>5</sub>
	3.40	—	1	—	$\pi$ -C <sub>5</sub> H <sub>5</sub>

\* Relative to SiMe<sub>4</sub> ( $\tau = 10$ ) as internal standard. † Estimated to nearest whole number by counting squares, rel. to  $\pi$ -C<sub>5</sub>H<sub>5</sub> = 5. ‡ Where multiplicity occurs which may be understood as first-order spin-spin couplings the splittings are recorded as the apparent coupling constants (app. *J*).

several different carbonyl species; however the only product so far isolated, in small yields, was the complex C<sub>5</sub>H<sub>5</sub>MoO<sub>2</sub>Cl (IV). Analytical data and the molecular weight are in accord with this formulation, as are the spectra. This compound forms diamagnetic yellow crystals, only slightly soluble in ether but very soluble in chloroform. Solutions and the solid are stable to atmospheric oxidation. The reaction is being further studied.

*Discussion.*—The allyl complexes are very similar in their properties to the related iron complexes,<sup>1</sup> and in many ways to the allyl compounds of manganese<sup>7</sup> and cobalt.<sup>8</sup>

<sup>7</sup> Heck and Breslow, *J. Amer. Chem. Soc.*, 1960, **82**, 750.

<sup>8</sup> Kaesz, King, and Stone, *Z. Naturforsch.*, 1960, **15b**, 682.

In the proton magnetic resonance spectrum of the  $\pi$ -allyl complex (II) the broadening of the doublet as assigned to the spectra of the  $H^3$  protons is unusual and has not been reported for numerous other  $\pi$ -allyl complexes,<sup>9</sup> even the closely related iron compounds.<sup>1</sup> It seems unlikely that external exchange processes could occur and the effect may be due to some interaction of the protons with the metal or other ligands.

The stability of the propene cations to hydrolysis, as noted for the related ethylene complexes,<sup>4</sup> is less for molybdenum than for the iron. The infrared spectrum of the propene cation shows weak absorption in the region 2800—3000  $cm^{-1}$  which may be assigned to the CH stretch of the methyl group. Therefore, there is a less marked reduction in the intensity of these bands than was observed for the spectra of the iron analogue.<sup>1</sup> The mechanism of the protonation of the  $\sigma$ -allyl complex (I), forming the propene cation (III), may be assumed to be similar to that already discussed for the iron system.<sup>1</sup> Ethylenic cations are, therefore, prepared both by proton addition to the allyl complex (I) and by hydride abstraction from the allyl complexes and it seems reasonable that these reactions may be general for suitable systems of other transition metals. The interest of the reversible conversion of these ethylenic cations into alkyl complexes, when considered in the light of mechanisms for the Fischer-Tropsch reaction and related systems, has been previously noted<sup>6</sup> and will be discussed in detail elsewhere.

The unusual molybdenyl complex (IV) is the second example of this class of complex, the first being cyclopentadienylvanadium oxide dichloride which was prepared analogously from  $C_5H_5V(CO)_4$ .<sup>10</sup> A considerable number of complexes in this class may doubtless be prepared. The molybdenyl complex (IV) is most simply regarded as containing hexivalent molybdenum, as in the oxychloride  $MoO_2Cl_2$ , and being essentially tetrahedral in configuration. A distorted tetrahedral structure for  $CrO_2Cl_2$  has been described.<sup>11</sup> If it is considered that the cyclopentadienyl group occupies three co-ordination positions then the metal can be viewed as being six-co-ordinate and octahedral by  $d^5s$ -hybridization, as discussed for the vanadyl complex.<sup>10</sup>

#### EXPERIMENTAL

Microanalyses were done in the Microanalytical Department, Lensfield Road, Cambridge. All preparations, reactions, and chromatographic separations were carried out in nitrogen or in a vacuum; solvents were degassed before use. Light petroleum was "AnalaR" material of b. p.  $<40^\circ$ .

*Tricarbonyl- $\sigma$ -allylcyclopentadienylmolybdenum.*—Sodium tricarbonylcyclopentadienylmolybdenate<sup>5</sup> (20 g.), from which volatile impurities such as unchanged  $Mo(CO)_6$  had been removed by sublimation, was dissolved in pure, dry tetrahydrofuran (150 ml.) and added slowly to a stirred solution of allyl chloride (20 ml., excess) in tetrahydrofuran (50 ml.). After  $1\frac{1}{2}$  hours' stirring, the solvent was removed under a vacuum and the product extracted with light petroleum. The extract was concentrated and chromatographed on an alumina column made up in light petroleum. The main yellow band which was eluted first with light petroleum was collected, the solvent removed, and the residual oil distilled at  $40^\circ/10^{-3}$  mm., to give the *complex* as a pale yellow oil, m. p.  $\sim -5^\circ$  (40%) [Found: C, 46.3; H, 3.5%; *M* (cryoscopic in benzene), 262.  $C_{11}H_{10}MoO_3$  requires C, 46.2; H, 3.5%; *M*, 286]. The complex decomposes rapidly in air, forming the binuclear compound  $[C_5H_5Mo(CO)_2]_2$ , blue material containing molybdenum, and unidentified hydrocarbons. It readily dissolves in common organic solvents and has a characteristic camphoraceous odour.

*Dicarbonyl- $\pi$ -allylcyclopentadienylmolybdenum.*—*Method I.* From the reaction mixture above, a second yellow band on the alumina column was removed by elution with ether. The solvent was removed from the eluate, giving deep yellow crystals which were twice recrystallized from ether-light petroleum and finally sublimed *in vacuo* at  $35^\circ$ . The yield of this *compound* was  $\sim 3\%$  [Found: C, 46.8; 46.2; H, 4.1, 3.5%; CO, 1.97 moles; *M* (cryoscopic in benzene), 296.  $C_{10}H_{10}MoO_2$  requires C, 46.5; H, 3.9%; CO, 2 moles; *M*, 258].

<sup>9</sup> Shaw and Sheppard, *Chem. and Ind.*, 1961, 517, and references therein.

<sup>10</sup> Fischer and Vigoureux, *Chem. Ber.*, 1958, **91**, 1342.

<sup>11</sup> Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 2360.

*Method II.* Pure tricarbonyl- $\sigma$ -allylcyclopentadienylmolybdenum (2.0 g.), in a quartz flask and under a high vacuum, was irradiated with intense ultraviolet light for 6 hr. The red semi-solid product was extracted with ether; the extract was concentrated and placed on an alumina column made up in light petroleum. Elution with light petroleum separated two yellow bands. The first band, eluted with light petroleum, was shown to contain unchanged  $\sigma$ -allyl complex. The second band was eluted with ether and the eluate was treated as in method I, giving the pure  $\pi$ -allyl complex (~50%).

Heating the pure  $\sigma$ -allyl complex under a vacuum at 60° for 4 hr., or refluxing a dilute solution of the  $\sigma$ -allyl complex in xylene for 2 hr., gave only small yields (~3%) of the  $\pi$ -allyl derivative.

The pure  $\pi$ -allyl complex is fairly stable in air; slight decomposition is noticeable after a day. It is very soluble in the common organic solvents; solutions when kept in air decompose within a few hours.

*Tricarbonylcyclopentadienyl-propenemolybdenum Salts.*—Tricarbonyl- $\sigma$ -allylcyclopentadienylmolybdenum (2 g.) in light petroleum (25 ml.) was treated with dry hydrogen chloride. A bright yellow precipitate was formed, which was extracted into water, in which it is very soluble. The solution was treated immediately with a concentrated solution of potassium hexafluorophosphate. The yellow precipitate of hexafluorophosphate was separated by filtration, washed with ether and water, dried under a vacuum, and finally recrystallized from liquid sulphur dioxide-ether (Found: C, 30.9, 29.9; H, 3.3, 2.9.  $C_{11}H_{11}F_6MoO_3P$  requires C, 30.6; H, 2.5%). The hexachloroplatinate was prepared in the same manner by using hexachloroplatinic acid (Found: C, 28.3; H, 2.9.  $C_{22}H_{22}Cl_6Mo_2O_6Pt$  requires C, 26.9; H, 2.4%).

If the petroleum solution of the  $\sigma$ -allyl complex is treated with an excess of hydrochloric acid, the yellow precipitate rapidly becomes red, forming the chloride  $C_5H_5Mo(CO)_3Cl$ , which was isolated and identified by its infrared spectrum. The initial yellow precipitate, shown to contain a propene group by its proton magnetic resonance spectrum, is presumably the chloride  $[C_5H_5Mo(CO)_2CH_2=CHMe]^+Cl^-$ . In aqueous solution the salt is rapidly hydrolysed, evolving propene. The hexafluorophosphate is discoloured in air after a few hours and also undergoes slow photochemical decomposition; however, it appears to be indefinitely stable when kept in the dark and under nitrogen.

*Tricarbonylcyclopentadienyl-1-deuteriopropenemolybdenum.*—Deuterium chloride was passed through a light petroleum solution of the  $\sigma$ -allyl complex (I). The deuterated hexafluorophosphate was precipitated and isolated as described above (Found: C, 30.2; H, 2.8.  $C_{11}H_{10}DF_6MoO_3P$  requires C, 30.5; H, 2.8%).

*Abstraction of a Hydride Ion from  $C_5H_5Mo(CO)_3C_2H_5$ .*—The ethyl complex <sup>2</sup> (VI) (0.8 g.), in solution in chloroform, was treated with a solution of triphenylmethyl fluoroborate (1 g.) in chloroform. The mixture changed from orange to dark red, and deep orange crystals were formed. After 10 min. the precipitated tetrafluoroborate of ion (VI) was filtered off, washed with chloroform, and recrystallized from acetone as golden crystals (~30%) (Found: C, 33.8; H, 2.4. Calc. for  $C_{10}H_9BF_4MoO_3$ : C, 33.5; H, 2.5%). The crystals are readily soluble in water and give precipitates such as hexafluorophosphate and reineckate (Found: C, 28.43; H, 2.7. Calc. for  $C_{14}H_{15}CrMoN_6O_3S_4$ : C, 28.5; H, 2.7%).

*Hydride Addition to  $[C_5H_5Mo(CO)_3C_2H_4]^+BF_4^-$  (IV).*—A suspension of the cation fluoroborate (IV) (0.2 g.) in tetrahydrofuran (25 ml.) was treated with a 10% excess of sodium borohydride. The mixture was stirred by a stream of nitrogen for 10 min. and then extracted with ether and water. The ether layer was separated, washed with water, and dried. The solvent was removed and the product sublimed *in vacuo* to give yellow crystals (30%) which were identified as the ethyl compound (V) from their infrared spectrum.

*Reaction of the  $\pi$ -Allyl Complex (II) with Hydrogen Chloride: Preparation of  $C_5H_5MoO_2Cl$ .*—Treatment of a petroleum solution of complex (II) (1.0 g. in 30 ml.) with a stream of hydrogen chloride for 20 min. gives a red precipitate. The precipitate was separated and extracted with chloroform in air, giving a yellow solution which decomposed slowly. The chloroform was removed and the residue sublimed to give a yellow-brown material which was extracted with ether. After being kept for 12 hr. in air, the ether was removed and the residue extracted and recrystallized several times from ether, affording yellow crystals [~3%, based on  $\pi$ -allyl complex (II)] of dioxochlorocyclopentadienylmolybdenum [Found: C, 26.3; H, 2.2; O, 14.8; Cl, 15.1; Mo, 41.8%; *M* (cryoscopic in benzene), 239.  $C_5H_5ClMoO_2$  requires C, 26.2; H, 2.2; O, 14.0; Cl, 15.1; Mo, 42.0; *M*, 228.5].

*Infrared Spectra.*—Measurements were made on a Perkin-Elmer model 21 spectrophotometer with sodium chloride optics. The spectra and some assignments are given below, except for the CO stretching frequencies which are given in Table 1. Mulls were in Nujol or hexachlorobutadiene; solutions were in carbon disulphide or tetrachloride.

$C_5H_5Mo(CO)_3\sigma-C_3H_5$  (film): 3904w, 3105w,\* 3077m, 2965m, 2930m, 2860m, 1760w, 1640w, 1612s,† 1550vw, 1427s, 1375vw, 1355w, 1298m, 1260vw, 1195s, 1108vw, 1060s, 1012s, 983s, 910m(sh), 879s, 810s, 735vw.

$C_5H_5Mo(CO)_2\pi-C_3H_5$  (soln.). 3900w, 3105w,\* 3060w, 3005w, 2970w, 2930w, 2862w, 1712vw, 1485w, 1460w, 1430w, 1384w, 1357vw, 1257m, 1221m, 1191m, 1105m, 1055m, 1007s, 937w, 898m, 825m (sh), 800s, 741m.

$[C_5H_5Mo(CO)_3CH_2=CH\cdot CH_3]^+PF_6^-$  (mull). 3110m,\*† 2990w, 2960w, 2920w, 2880w, 2850w, 2780vw, 2480vw, 2440vw, 2400vw, 2260vw, 1507vw,§ 1463m, 1438m, 1421m, 1408w, 1382m, 1361w, 1298vw, 1236w, 1110w, 1070vw, 1035m, 910vw, 866s, 840s ( $PF_6^-$ ), 821s, 775vw.

$[C_5H_5Mo(CO)_3CH_2=CH\cdot CH_2D]^+PF_6^-$  (mull). 3080m,\* 2920w, 2860w, 2800w, 2720vw, 2460vw, 2400vw, 2380vw, 2200vw, 1506vw,§ 1462w, 1431w, 1420m, 1408m, 1382w, 1360m, 1296m, 1275m, 1233w, 1150vw, 1110w, 1070vw, 1035m, 1020m, 1004m, 860vs ( $PF_6^-$ ).

$C_5H_5MoO_2Cl$  (soln.). 3100w,\* 2840vw, 1887vw, 1785vw, 1457m, 1421m, 1360w, 1260vw, 1070vw, 1024m, 1001m, 920s, 887s, 830s.

$[C_5H_5Mo(CO)_3C_2H_4]^+PF_6^-$  (mull). 3105m,\* 1514vw,§ 1446m, 1434m, 1416m, 1359w, 1300w, 1225m, 1112w, 1020w, 1004w, 954w, 840vs ( $PF_6^-$ ).

*Nuclear Magnetic Resonance Spectra.*—Measurements were made on a Perkin-Elmer spectrophotometer at 40 Mc./sec. at room temperature. The spectra and conditions of measurement are given in Table 2.

We thank The Ethyl Corporation for a gift of molybdenum carbonyl, Dr. N. Sheppard and Mr. E. Liddell for assistance with the spectra, and Unilever Ltd. for financial support (to M. C.).

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[Received, July 30th, 1962.]

\* C-H stretch of  $\pi-C_5H_5$ . † Unco-ordinated C=C stretch. ‡ Olefinic C-H stretch. § Co-ordinated C=C stretch.