Arene Molybdenum Chemistry: Some Bis-π-allylic Derivatives

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The preparation and properties of the bis-π-allyl derivatives $(C_6H_5R)Mo(\pi\text{-}C_3H_5)_2$ are described. The butadiene cation $[C_6H_6Mo(\pi\text{-}C_3H_5)C_4H_6]^+$ reacts readily with nucleophiles (Nu = CN, OMe, SMe, H) to give the neutral π-allylic derivatives $C_6H_6Mo(\pi\text{-}C_3H_5)(\pi\text{-}NuCH_2C_3H_4)$.

SINCE the π-allyl ligands of bis-π-allylnickel are readily displaced by olefins to give nickel catalysts,[1] it seemed possible that bis-π-allyl(benzene)molybdenum might show similar properties. The preparation of this, and related systems have therefore been attempted, as described below. Some parts of this work have been briefly communicated.[2]

Chemical Studies.—Treatment of the binuclear compounds $[(RC_6H_5)Mo(\pi\text{-}C_3H_5)Cl]_2$ [3] (I; R = H, Me) in dry tetrahydrofuran with an excess of allylmagnesium chloride gave volatile orange crystalline compounds. The data given in the Table and the Experimental section strongly suggest they have the formulation $(RC_6H_5)Mo(\pi\text{-}C_3H_5)_2$ (II; R = H, Me) with the structures shown in the Scheme. The compounds (II) are moderately soluble in light petroleum and ethanol and very soluble in benzene, chloroform, and ether; they are insoluble in water. Solutions showed decomposition after exposure to air within a few minutes but the crystals only showed signs of oxidation after an hour. In contrast to the well-known reactivity of bis-π-allyl-nickel, the compounds (II) failed to react with dimethylphenylphosphine or ethylenediamine during 6 h at 90° and starting materials were recovered. With allyl chloride the compound (II; R = H) reacted slowly but the only identified product was hexa-1,5-diene (g.l.c.). Smooth reactions were observed with the compound (II; R = Me) and 1 equiv. of some carboxylic acids according to the following equation:

$$(MeC_6H_5)Mo(\pi\text{-}C_3H_5)_2 + R'CO_2H \longrightarrow (MeC_6H_5)Mo(\pi\text{-}C_3H_5)(O_2CR') + MeCH{=}CH_2 \quad R' = H, Me\ or\ Ph$$

The carboxylato-derivatives were identified by comparison of their i.r. spectra with authentic samples.[4]

Treatment of the compounds (II) with an excess of the acids $R'CO_2H$ (R' = Me or CF_3) gave the well-known dimers $[Mo(O_2CR')_2]_2$ [5] in good yield.

Compound (II; R = H) was recovered unchanged from a solution of butyl-lithium in hexane. Further, it failed to react with methyl iodide in light petroleum during 2 days. The butadiene derivative $[C_6H_6Mo(\pi\text{-}C_3H_5)(C_4H_6)]^+BF_4^-$ (III) [2] reacted readily with nucleophiles Nu^- giving bis-π-allylic compounds which are closely related to the complexes (II). Thus, treatment of compound (III) with sodium borohydride gave an orange complex the data for which (see Table and Experimental section) suggest it is the π-methylallyl derivative $C_6H_6Mo(\pi\text{-}C_3H_5)(\pi\text{-}NuCH_2C_3H_4)$ (IV; Nu = H). In particular, the ^1H n.m.r. spectrum determined at 270 MHz allows clear assignment corresponding to the structure given in the Scheme.

The butadiene compound (III) also reacted rapidly with the anions OMe^-, SMe^-, or CN^- giving the analogues (IV; Nu = OMe, SMe, or CN) in good yield. Again the ^1H n.m.r. spectra provided strong evidence for the proposed structures. Treatment of the methoxy-derivative (IV; Nu = OMe) in benzene with acetic acid reformed the parent butadiene cation (III) which was isolated as the hexafluorophosphate salt and identified from its i.r. spectrum. In contrast, the crotyl derivative (IV; Nu = H) behaved in the same way with glacial acetic acid as the bis-π-allyl analogue (II; Nu = H). Reaction of stoicheiometric quantities gave the acetate derivative $C_6H_6Mo(\pi\text{-}C_3H_5)O_2CMe$, whilst an excess of the acid gave the dimer $[Mo(O_2CMe)_2]_2$.

DISCUSSION

It appears that the bis-π-allyl compounds (II) and (IV; Nu = H) are resistant to nucleophilic attack, and to ligands such as tertiary phosphines. This behaviour contrasts markedly with the labile bis-π-allyl nickel. The lower reactivity of the molybdenum compounds may be associated with the higher degree of co-ordination compared with the 16-electron nickel system.

Nucleophilic attack on the butadiene cation $[C_6H_6Mo(\pi\text{-}C_3H_5)C_4H_6]^+$ could be envisaged to occur on any one of the three organic ligands. Attack on the π-allyl group, giving a zero-valent, olefin product, might not be expected since it would be very electron rich. However, nucleophilic addition to either the benzene or butadiene ligands would give divalent products, namely cyclohexadienyl or π-allylic derivatives respectively. The former products have been shown to be formed by nucleophilic attack on the benzene cations $[C_6H_6Mo(\pi\text{-}C_3H_5)L_2]^+$, where $L_2 = Me_2P(CH_2)_2PMe_2$.[6] The fact that, as shown above, nucleophilic addition occurs on the butadiene ring may not be simply understood. It may be due to a relatively smaller loss of ligand conjugation than if the benzene ligand was converted into a hexadienyl system.

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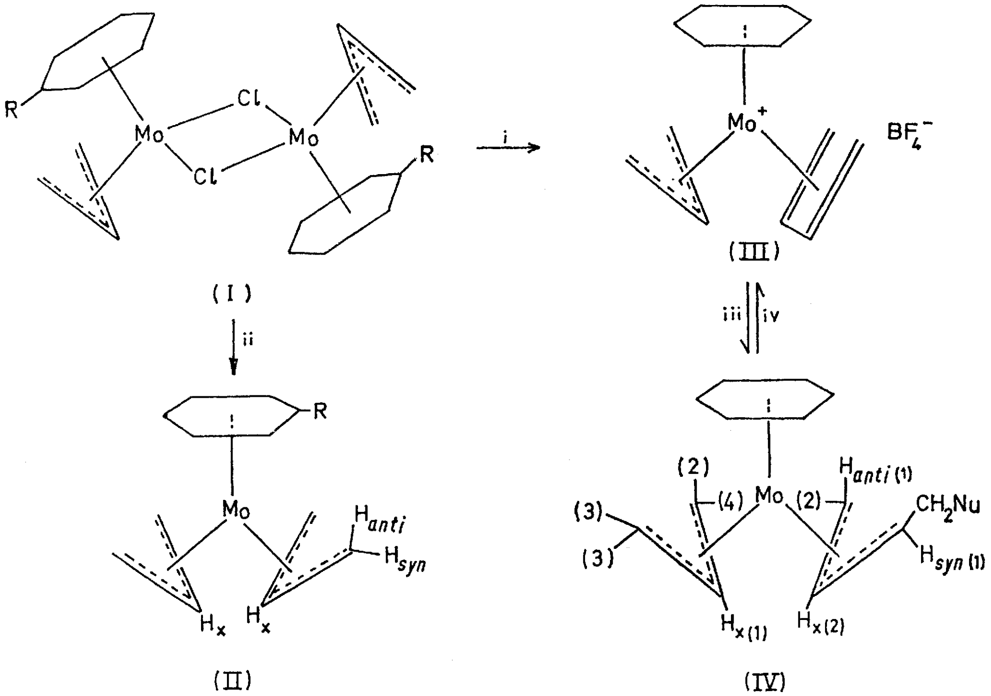
[4] M. L. H. Green, L. C. Mitchard, and W. E. Silverthorn, *J.C.S. Dalton*, 1973, 1403.

[5] E. Bannister, T. A. Stevenson, and G. Wilkinson, *J. Chem. Soc.*, 1964, 2538.

[6] M. L. H. Green, L. C. Mitchard, and W. E. Silverthorn, *J.C.S. Dalton*, 1973, in the press.

EXPERIMENTAL

Preparations and isolation procedures were carried out under a nitrogen atmosphere or *in vacuo*. Tetrahydrofuran, diethyl ether, benzene, and dichloromethane were dried by refluxing over finely ground calcium hydride followed by distillation. Light petroleum refers to AnalaR grade, b.p. 30—40°. The dimers $[(C_6H_5R)Mo(\pi\text{-}C_3H_5)Cl]_2$ (R = H, Me) were prepared as previously described. I.r. spectra were determined using a Perkin-Elmer 457 instrument. ^1H N.m.r. spectra were determined at 60 MHz on a JEOLC-60-HL instrument, at 100 MHz on a Perkin-Elmer 100 MHz instrument and at 270 MHz on a Bruker instrument.



SCHEME Reagents: i, C_4H_6, $TlBF_4$, acetone; ii, C_3H_5MgCl, R = H or Me; iii, Nu^-=H^-, OMe^-, SMe^-, CN^-; iv, H^+, Nu = OMe

Compound	Colour	Analytical data (%) Found (reqd.)		Mass [a] spectra	Selected i.r. data [b]
$C_6H_6Mo(\pi\text{-}C_3H_5)_2$	Orange-yellow	55·9(56·2)	6·5(6·2)	258	3050m,[c] 1530w [d]
$MeC_6H_5Mo(\pi\text{-}C_3H_5)_2$	Orange-yellow	58·0(57·8)	6·7(6·7)	272	3050m,[c] 1530w [d]
$C_6H_6Mo(\pi\text{-}C_3H_5)(\pi\text{-}1\text{-}MeC_3H_4)$	Orange	57·3(57·7)	6·8(6·7)	272	3080m,[c] 1530w [d]
$C_6H_6Mo(\pi\text{-}C_3H_5)[\pi\text{-}1\text{-}(CH_2OMe)C_3H_4]$	Orange	55·8(56·0)	7·0(6·7)	302	3070m,[c] 1540w,[d] 1075vs [e]
$C_6H_6Mo(\pi\text{-}C_3H_5)[\pi\text{-}1\text{-}(CH_2CN)C_3H_4]$	Orange	56·4(56·9)	5·8(5·8) [f]	297	3040w,[c] 2245m,[g] 1530w [d]
$C_6H_6Mo(\pi\text{-}C_3H_5)[\pi\text{-}1\text{-}(CH_2SMe)C_3H_4]$	Dark red	53·1(53·2)	6·7(6·4) [h]		3070m,[c] 1530w [d]

[a] Parent ion peak for ^{98}Mo isotope. [b] Nujol mulls, calibrated with polystyrene film. [c] CH str. [d] CC str. of π-allyl. [e] CO str. [f] %N, 4·3(4·6). [g] νC≡N. [h] %S, 11·1(10·1).

All spectra were calibrated using tetramethylsilane as internal standard. Mass spectra were measured on an AEI MS4 instrument.

Bis-π-allyl(benzene)molybdenum.—The dimer $[C_6H_6Mo(\pi\text{-}C_3H_5)Cl]_2$ (0·50 g, 1·0 mmol) in dry tetrahydrofuran (50 ml) was treated with an excess of freshly prepared allylmagnesium chloride (1M; 2 mmol) in diethyl ether. The mixture was stirred for 2 h during which time the solution became deep red and the dimer dissolved. After the mixture had been cooled to −30° a few drops of water were added slowly to it in order to hydrolyse the excess of Grignard reagent. The product was warmed and the solution was filtered; the solvent was removed from the deep red filtrate under reduced pressure to give a brown solid which was then extracted with light petroleum (30 ml.) The extract was filtered and the filtrate was cooled slowly to −25° to give brown needles. These were sublimed at 110°/10^{-3} mmHg to give deep orange crystals of the pure compound (yield *ca* 45%).

The toluene analogue, $(C_6H_5Me)Mo(\pi\text{-}C_3H_5)_2$ was similarly prepared starting from the toluene dimer $[(C_6H_5Me)Mo(\pi\text{-}C_3H_5)Cl]_2$ except that the reaction time was ½ h (yield *ca* 60%).

π-1-Cyanocrotyl-π-allyl(benzene)molybdenum.—The compound butadiene-π-allyl(benzene)molybdenum tetrafluoroborate (0·35 g, 1·0 mmol) in water (20 ml) was treated with sodium cyanide (0·12 g, 2·0 mmol) and the mixture was stirred at 90° for 2 h. A yellow solid separated from the solution and this was extracted with benzene (20 ml); the benzene was removed from the extract under reduced pressure. The residue was extracted with hot, light petroleum (b.p. 60—80°) (10 ml) and the extract was filtered to give an orange filtrate; this was allowed to cool slowly to room temperature to give orange crystals. These were recrystallised from light petroleum as before and finally washed with cold, light petroleum and dried *in vacuo* (yield *ca* 30%).

π-1-Methoxycrotyl-π-allyl(benzene)molybdenum.—The compound $[C_6H_6Mo(\pi\text{-}C_3H_5)C_4H_6]^+$ BF_4^- (0·35 g, 1·0 mmol) in pure methanol (15 ml) was treated with sodium methoxide (0·5 g) and the solution was warmed to 60° for 10 min with stirring. The orange suspension dissolved to give a green-yellow solution. The solvent was removed *in vacuo* and the dark residue was washed with water (5 ml). The residue was dried and extracted with light petroleum (20 ml). The extract was filtered to give an orange filtrate which was cooled slowly to 0° to give large orange crystals. These were recrystallised again from light petroleum, and finally dried *in vacuo* (yield *ca* 50%).

π-Crotyl-π-allyl(benzene)molybdenum.—The compound $[C_6H_6Mo(\pi\text{-}C_3H_5)C_4H_6]^+BF_4^-$ (0·7 g, 2·0 mmol) in tetrahydrofuran (15 ml) was treated with sodium borohydride (0·50 g) and the solution was stirred at room temperature for 30 min. Effervescence was observed and the mixture became dark with deposition of a black solid. The mixture was filtered to give a dark red filtrate from which the solvent was removed under reduced pressure. The dark residue was washed with water (5 ml) and then dried and then extracted with light petroleum (5 ml). The extract was filtered to give an orange filtrate which was cooled to −10° to give orange crystals. These were dried and sublimed *in vacuo* at 75° and finally recrystallised from light petroleum at −10° yield (*ca.* 30%).

π-1-*Methylthiocrotyl-π-allyl(benzene)molybdenum.*—The compound $[C_6H_6Mo(\pi\text{-}C_3H_5)C_4H_6]^+BF_4^-$ (0·71 g, 2·0 mmol) in ethanol (15 ml) was treated with a freshly prepared solution of sodium methanethiolate in ethanol [0·4 g in ethanol (20 ml.)] and the mixture was stirred at room temperature. The solution became red after a few min and a dark red solid was slowly deposited. The mixture was warmed to 50°, when the solid dissolved. After 30 min the solvent was removed under reduced pressure and the dark red residue was extracted with benzene (20 ml). The extract was filtered and the solvent was removed under reduced pressure. The residue was extracted with hot, light petroleum (b.p. 60—80°; 30 ml.) and the extract was filtered and then concentrated to *ca.* 15 ml. When slowly cooled to −20° it gave dark red crystals of the pure compound (yield *ca.* 55%).

Reaction of $C_6H_6Mo(\pi\text{-}C_3H_5)(\pi\text{-}1\text{-}MeOCH_2C_3H_4)$ *with Hydrochloric Acid.*—The compound π-1-methoxycrotyl-π-allyl(benzene)molybdenum (0·3 g, 1·0 mmol) in water (10 ml) was treated with concentrated hydrochloric acid (1·0 ml). The mixture was stirred at room temperature and after 2 min the solution became orange and the solid dissolved. The solution was filtered and a few drops of saturated aqueous ammonium hexafluorophosphate were added to the filtrate. The orange precipitate which separated was collected and washed with water and finally recrystallised from acetone–water. The orange crystals were identified from the i.r. spectrum as the butadiene derivative $[C_6H_6Mo(\pi\text{-}C_3H_5)C_4H_6]^+PF_6^-$ (yield *ca.* 80%). The same reaction was observed if the hydrochloric acid was replaced by acetic acid.

^1H *N.m.r. Data.*—Data are presented as: chemical shift, relative intensity, multiplicity (J in Hz), assignment. Solutions were in $[^2H_6]$ benzene. The labelling of the hydrogens is shown in the Scheme.

$C_6H_6Mo(\pi\text{-}C_3H_5)_2$ (at 60 MHz): 6·00, 6, s, C_6H_6; 6·60, 2, c, H_x; 8·15, 4, d (J = 7·50), H_{syn}; 8·90, 4, d (J = 10·5) H_{anti}.

$MeC_6H_5Mo(\pi\text{-}C_3H_5)_2$ (at 60 MHz): 6·15, 5, c, Ph; 6·65, 2, c, H_x; 8·15, 4, d (J = 7·50); H_{syn} 8·75, 3, s, Me; 9·10, 4, d (J = 9·95) H_{anti}.

$C_6H_6Mo(\pi\text{-}C_3H_5)(\pi\text{-}1\text{-}MeC_3H_4)$ (at 270 MHz). 5·90, 6, s, C_6H_6; 6·15, 1, tt, H_x; 6·50, 1, broad quart, H_d; 8·0—8·2, 3, two 1 : 1, d (J = 7·7) superimposed on a multiplet, $H_{syn(1)}$, $H_{syn(3)}$ *a*, $H_{syn(4)}$ *a*; 8·28, 1, d (J = 7·75) $H_{syn(2)}$; 8·45, 3, d (J = 6·20) Me; 8·85, 2, overlapping doublets (J = 10·05) $H_{anti(2)}$ a, $H_{anti(3)}$ *a*; 9·05, 1, d (J = 10·05) $H_{anti(1)}$ *b*. (*a*, Appears as a singlet when H_x is irradiated. *b*, Appears as a singlet when H_d is irradiated.)

$C_6H_6Mo(\pi\text{-}C_3H_5)(\pi\text{-}1\text{-}(CH_2OMe)C_3H_4)$ (at 270 MHz): 5·8, 6, s, C_6H_6; 6·6, 2, c, $H_{x(1)}$, $H_{x(2)}$; 6·75, 3, s, Me; 7·30, 1, broad t (J = 10·5) $H_{syn(1)}$; 7·80, 3, overlapping doublets $H_{syn(2)}$, CH_2; 8·00, 1, d (J = 7·50), 8·15, 1, d (J = 7·50) $H_{syn(3)}$, $H_{syn(4)}$; 8·65, 3, overlapping doublets, $H_{anti(1)}$, $H_{anti(2)}$, $H_{anti(3)}$.

$C_6H_6Mo(\pi\text{-}C_3H_5)(\pi\text{-}1\text{-}(CH_2CN)C_3H_4)$ (at 60 MHz): 6·15, 6, s, C_6H_6; 6·7—9·2, *ca* 11, c, $\pi\text{-}C_3H_5$, $\pi\text{-}C_3H_4CH_2$.

$C_6H_6Mo(\pi\text{-}C_3H_5)(\pi\text{-}1\text{-}(CH_2SMe)C_3H_5)$ (at 270 MH_2): 5·95, 6, s, C_6H_6; 6·60, 1, c, $H_{x(1)}$; 6·80, 1, c, $H_{x(2)}$; 7·40, 1, broad t (J = 10·0) $H_{syn(1)}$, 7·60, 1, d (J = 12·80), 7·90, 1, d (J = 8·50) $H_{syn(2)}$, $H_{syn(3)}$; 7·95, 3, s, Me; 8·15, 1, d (J = 8·40) $H_{syn(4)}$; 8·25, 1, d (J = 8·40), 8·65, 1, c, 8·85, 3, d (J = 10·50), $H_{anti(1)}$, $H_{anti(2)}$, CH_2, $H_{anti(3)}$.

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