Arene Molybdenum Chemistry: Arene(π-allyl)molybdenum Derivatives Containing Carboxylate, Aminocarboxylate, and Related Ligands

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The carboxylato-compounds benzene Mo(π-C_3H_5)L, where L = O_2CH, O_2CMe, O_2CPh, $O_2CCH_2[Fe(CO)_2(\pi$-(π-$C_5H_5)]$, and related derivatives are described. The complexes where L = $NH_2CH_2CO_2$ or $NH_2[CH_2]_2S$ have been prepared. The latter reacts with methyl iodide forming the cation $\{C_6H_6Mo(\pi\text{-}C_3H_5)(MeS[CH_2]_2NH_2)\}^+$. β-Diketone derivatives where L= MeCOCHCOMe or MeCOCHCO(OEt) have also been isolated.

In view of the difficulty of predicting the reactivity of a system such as (arene)Mo(π-C_3H_5) it was decided to attempt to prepare a variety of derivatives in order to better understand its nature. We have found that the chloro-dimers [(arene)Mo(π-C_3H_5)Cl]$_2$ are convenient starting materials for a number of neutral 18-electron complexes of the general type (arene)Mo(π-C_3H_5)L, where L represents three-electron ligands such as carboxylate, acetylacetonate, and related systems. Part of this work has been briefly communicated.[1]

Chemical Studies.—(a) *Carboxylato-derivatives.* Treatment of bisbenzenemolybdenum with allyl acetate results in a smooth oxidative replacement–addition reaction giving a purple crystalline compound which the data given in the Table shows to be the monomer C_6H_6Mo(π-C_3H_5)O_2CR (II; R = Me). The same compound may also be prepared by addition of one mol of acetic acid to the bis-π-allyl compound C_6H_6Mo(π-C_3H_5)$_2$[1] and propene is evolved during the reaction, *viz*:

$$C_6H_6Mo(\pi\text{-}C_3H_5)_2 + MeCO_2H \longrightarrow C_6H_6Mo(\pi\text{-}C_3H_5)O_2CMe + MeCH{=}CH_2$$

The compounds (II; R = H or Ph) are formed similarly using stoicheiometric quantities of formic or benzoic acid. No reaction was observed with the acid (π-C_5H_5)-Fe(CO)$_2$CH$_2$COOH, presumably because this is a very weak acid,[2] and with 4-chloro-3,5-dinitrobenzoic acid decomposition followed a rapid reaction and no tractable molybdenum products were isolated.

The most convenient route to the compounds (II) is *via* treatment of the chloro-dimer (I) in ethanol with sodium or potassium salts of the carboxylic acids. The derivatives of (II), where R = H, Me, Ph, π-C_5H_5Fe(CO)$_2$CH$_2$, *p*-[(π-C_5H_5)Fe(CO)$_2$]COC$_6$H$_4$, (π-C_5H_5)Mo(CO)$_3$CH$_2$, (EtO)-COCH$_2$, and *p*-substituted benzoates have been prepared this way. The reactions are shown in the Scheme and the evidence for their formulations is given in the Table and is discussed in part below.

The formato-compound (II; R = H) forms purple

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[1] M. L. H. Green, J. Knight, L. C. Mitchard, G. G. Roberts, and W. E. Silverthorn, *Chem. Comm.*, 1971, 1619.

[2] J. K. P. Ariyaratne, A. M. Bierrum, M. L. H. Green, M. Ishaq, C. K. Prout, and M. G. Swanwick, *J. Chem. Soc.* (*A*), 1969, 1309.

crystals, m.p. 92—93°, which are soluble in benzene and aqueous ethanol. Solutions show decomposition within hours on exposure to air but are stable under nitrogen. Most other compounds (II) show similar appearance and stability to oxidation. Treatment of the compounds (II) with hydrochloric acid or hydrogen chloride gas does not reform the dimer (I). Rather the π-allyl group is attacked and propene is evolved. No other tractable products could be isolated. In contrast, treatment of the complexes (II; R = Me or Ph) with an excess of the corresponding acid RCO_2H gives propene and the previously described dimers $[Mo(RCO_2)_2]_2$.[3,4] In fact, treatment of the bis-π-allyl compound $C_6H_6Mo(\pi\text{-}C_3H_5)_2$ with an excess of the acids RCOOH gives the carboxylato-dimers in essentially quantitative yields, when R = Me, CF_3, or Ph.

Analytical and spectroscopic data

Compound	Colour	Analytical data, % (reqd.) C	H	M^+/e [a]	Selected i.r. data (mulls)	^1H N.m.r. data [b]
$(C_6H_6)Mo(\pi\text{-}C_3H_5)O_2CH$	Purple	45·9 (46·2)	4·7 (4·6)	262	1550s ^{c,d}	2·55, **1**, s, CH; 6·10, **6**, s;^{e} 6·40, **1**, c;^{f} 7·15, **2**, d (J 6·35);^{g} 7·90, **2**, d (J 8·25) ^{h,i}
$(C_6H_6)Mo(\pi\text{-}C_3H_5)O_2CMe$ ^{j}	Purple	49·8 (50·0)	5·3 (5·5)	276	1515s ^{c}	5·85, **6**, s;^{e} 6·40, **1**, c;^{f} 7·08, **2**, d (J 6·05);^{g} 7·81, **2**, d (J 8·25);^{h} 8·45, **3**, s, Me ^{i}
$(C_6H_6)Mo(\pi\text{-}C_3H_5)O_2CPh$	Golden	57·2 (57·1)	4·8 (4·8)	338	1530sh,^{d} 1510s ^{c}	2·00, **2**, c, 3·15, **3**, c, Ph; 6·05, **6**, s;^{e} 6·40, **1**, c;^{f} 7·08, **2**, d (J 6·45);^{g} 7·92, **2**, d (J 7·80) ^{h,i}
$(C_6H_6)Mo(\pi\text{-}C_3H_5)(p\text{-}O_2CC_6H_4CO_2Me)$	Purple	54·4 (54·9)	4·3 (4·6)	396	1530sh,^{d} 1505s ^{c}	2·15, **4**, c, Ph; 6·00, **6**, s;^{e} 6·50, **1**, c; ^{f}6·75, **3**, s, Me; 7·05, **2**, d (J 6·37);^{g} 7·90, **2**, d (J 7·50) ^{h,i}
$(C_6H_6)Mo(\pi\text{-}C_3H_5)O_2CCH_2CO_2Et$	Purple	48·3 48·8)	5·3 (5·2)	348	1540s ^{c,d}	5·90, **6**, s;^{e} 6·20, **3**, q (J 7·50), O–CH_2 and H_c; 7·15, **4**, s, $COCH_2$ and d (J 6·75);^{g} 7·85, **2**, d (J 8·25);^{h} 9·20 **3**, t (J 7·50) Me ^{i,k}
$(C_6H_6)Mo(\pi\text{-}C_3H_5)O_2CCH_2Fe(CO)_2\text{-}(\pi\text{-}C_5H_5)$	Dark red	47·7 (48·0)	3·9 (4·0)	452	2040vs,^{l} 1960vs,^{l} 1540m,^{c} 1525sh ^{d}	4·65, **5**, s, $\pi\text{-}C_5H_5$; 4·85, **6**, s;^{e} 6·25, **1**, c;^{f} 6·92, **2**, d (J 6·35);^{g} 7·40, **2**, d (J 7·65);^{h} 8·30, **2**, s, CH_2 ^{m}
$(C_6H_6)Mo(\pi\text{-}C_3H_5)\{p\text{-}O_2CC_6H_4COFe\text{-}(CO)_2(\pi\text{-}C_5H_5)\}$	Dark red	53·5 (53·4)	3·9 (3·7)		2040vs,^{l} 1960vs,^{l} 1615s,^{n} 1535w,^{d} 1510s ^{c}	1·65, **2**, c, 2·15, **2**, c, C_6H_4; 4·60, **5**, s, $\pi\text{-}C_5H_5$; 4·80, **6**, s;^{e} 6·25, **1**, c;^{f} 6·75, **2**, d (J 6·75);^{g} 7·25, **2**, d (J 7·50) ^{h,m}
$(C_6H_6)Mo(\pi\text{-}C_3H_5)O_2CCH_2Mo(CO)_3\text{-}(\pi\text{-}C_5H_5)$	Dark red	43·7 (44·0)	3·6 (3·5)		2040vs,^{l} 1930vs,^{l} 1855m,^{l} 1535w ^{d}	5·45, **5**, s, $\pi\text{-}C_5H_5$; 5·95, **6**, s;^{e} 6·55, **1**, c;^{f} 7·25, **2**, d (J 6·75);^{g} 8·00, **2**, d (J 7·85);^{h} 8·62, **2**, s, CH_2 ^{i}
$\mu\text{-}C_2O_4\text{-}[(C_6H_6)Mo(\pi\text{-}C_3H_5)]_2$	Dark red	45·9 (46·3)	4·2 (4·3)	522	1640vs,^{o} 1530m ^{d}	6·15, **6**, s;^{e} 7·3, **2**, d (J 4·5);^{g} 7'90, **2**, d (J 7·5) ^{h,i,p}
$(C_6H_6)Mo(\pi\text{-}C_3H_5)NH_2CH_2CO_2$	Pink-purple	45·2 (45·7)	5·0 (5·2) ^{q}	291	3300m,^{r} 3250sh,^{r} 3160m,^{r} 1600s,^{c} 1535w,^{d} 1400m ^{s}	
$(MeC_6H_5)Mo(\pi\text{-}C_3H_5)NH_2CH_2CO_2$	Pink-purple	47·2 (47·5)	5·5 (5·6) ^{t}		3295m,^{r} 3240m,^{r} 3160m,^{r} 1600s,^{c} 1540w ^{d}	
$(C_6H_6)Mo(\pi\text{-}C_3H_5)NH_2[CH_2]_2S$	Purple	45·2 (45·4)	6·2 (5·9) ^{v}	293	3300m,^{r} 3180m,^{r} 3090s,^{r} 1590m,^{u} 1530w ^{d}	
$(MeC_6H_5)Mo(\pi\text{-}C_3H_5)NH_2[CH_2]_2S$	Purple	46·9 (47·2)	6·2 (6·2) ^{w}		3300m,^{r} 3180m,^{r} 3090s,^{r} 1590m,^{u} 1530m ^{d}	
$[(C_6H_6)Mo(\pi\text{-}C_3H_5)NH_2[CH_2]_2SMe]^+PF_6^-$	Dark red	31·8 (32·0)	4·6 (4·5) ^{x}		3360m,^{r} 3310m,^{r} 1600m,^{u} 1530w ^{d}	4·52, **6**, s;^{e} 6·20—7·8, **13**, c;^{y} 8·34, **1**, d (J 7·50) ^{h}
$(C_6H_6)Mo(\pi\text{-}C_3H_5)MeCO{\cdot}CH{\cdot}COMe$	Dark red	53·5 (53·5)	5·5 (5·7)	316	1580vs ^{z} 1530s ^{o}	4·92, **1**, s, CH; 5·90, **6**, s;^{e} 6·25, **1**, **9** (J 7·4, 6·2); 7·61, **2**, d (J 7·40);^{g} 7·65, **2**, d (J 6·2);^{h} 8·32, **6**, s, Me_2 ^{i,k}
$(C_6H_6)Mo(\pi\text{-}C_3H_5)MeCO{\cdot}CH{\cdot}CO(OEt)$	Pink	52·3 (52·3)	5·6 (5·8)	346	1620vs,^{z} 1510s ^{o}	5·05, **1**, s, CH; 5·28, **6**, s;^{e} 6·15, **3**, c, H_c and O–CH_2 (J 7·50); 7·6, **4**, c;^{g,h} 8·21, **3**, s, C–Me; 9·02, **3**, t (J 7·50) CH_2–*Me* ^{i}

[a] Parent ion peak, ^{98}Mo isotope. [b] Given as: chemical shift (τ), **relative intensity**, multiplicity (J in Hz), assignment, *etc.* Measured at 60 MHz. [c] ν(C–O) Antisymmetric stretch. [d] ν(C–C) stretch of π-allyl group. [e] C_6H_6 Hydrogens. [f] H_c (See Scheme). [g] H_{syn}. [h] H_{anti}. [i] In $[^2H_6]$benzene. [j] M (benzene) 273 (274). [k] Also measured at 100 MHz. [l] ν(C≡O) stretch. [m] In $[^2H]$chloroform. [n] ν(C⩦O) of Fe–CO–C_6H_4–. [o] ν(C=O). [p] Dilute soln. H_c not detected. Also seen, a weak band at τ 6·07, see text. [q] N, 4·6 (4·85)%. [r] ν(N–H). [s] ν(C=O) symmetric stretch. [t] N, 4·7 (4·6)%. [u] δ(N–H) bend. [v] N, 4·5 (4·8)%. [w] N, 4·5 (4·6)%. [x] N, 3·1 (3·1)%. [y] In $[^2H_6]$dimethyl sulphoxide; complex spectrum. [z] ν(C⩦C) stretch of acetylacetonate group.

The ^1H n.m.r. spectra of the complexes (II) provide unambiguous evidence for the presence of a (benzene)-$Mo(\pi\text{-}C_3H_5)$ group. The i.r. spectra show bands characteristic of a π-allyl group, near 1530 cm^{-1}, and of a carboxylato-system, such as the antisymmetric stretching frequency near 1520 cm^{-1}. Bands characteristic of a normal ester C=O stretching frequency are absent. The mass spectra show parent ions peaks in all cases which correspond to a monomeric formulation. Therefore, it is proposed that the compounds (II) have the structures shown in the Scheme, where the carboxylato-group acts as a three-electron ligand to the molybdenum. We are unable to find another example of a terminal formato-ligand in the literature. It is clear from the above that the $(benzene)Mo(\pi\text{-}C_3H_5)$ system shows a marked affinity for the terminal carboxylato-ligand. Treatment of the dimer (I) with the disodium salt of oxalic acid gives a dark red crystalline product with stoicheiometry corresponding to the binuclear compound $\mu\text{-}C_2O_4\text{-}[C_6H_6Mo(\pi\text{-}C_3H_5)]_2$, ($M^+/e$ 522). It is only slightly soluble in benzene and chloroform, in which it slowly decomposes. The ^1H n.m.r. spectra in both solvents showed a small band close to the main band assignable to the C_6H_6 hydrogens and this may be due to an isomer. Attempts to separate or further purify the product were unsuccessful since recrystallisation from various solvents gave the same result and the compound decomposed during chromatography on alumina. The product formed by treatment of the bis-π-allyl compound $C_6H_6Mo(\pi\text{-}C_3H_5)_2$ with oxalic acid was identical to the binuclear compound, including the ^1H n.m.r. spectrum. Variable temperature spectra showed little change between −65 and +60°.

Four isomers may be envisaged for the binuclear compound, excluding positional isomers of the π-allyl

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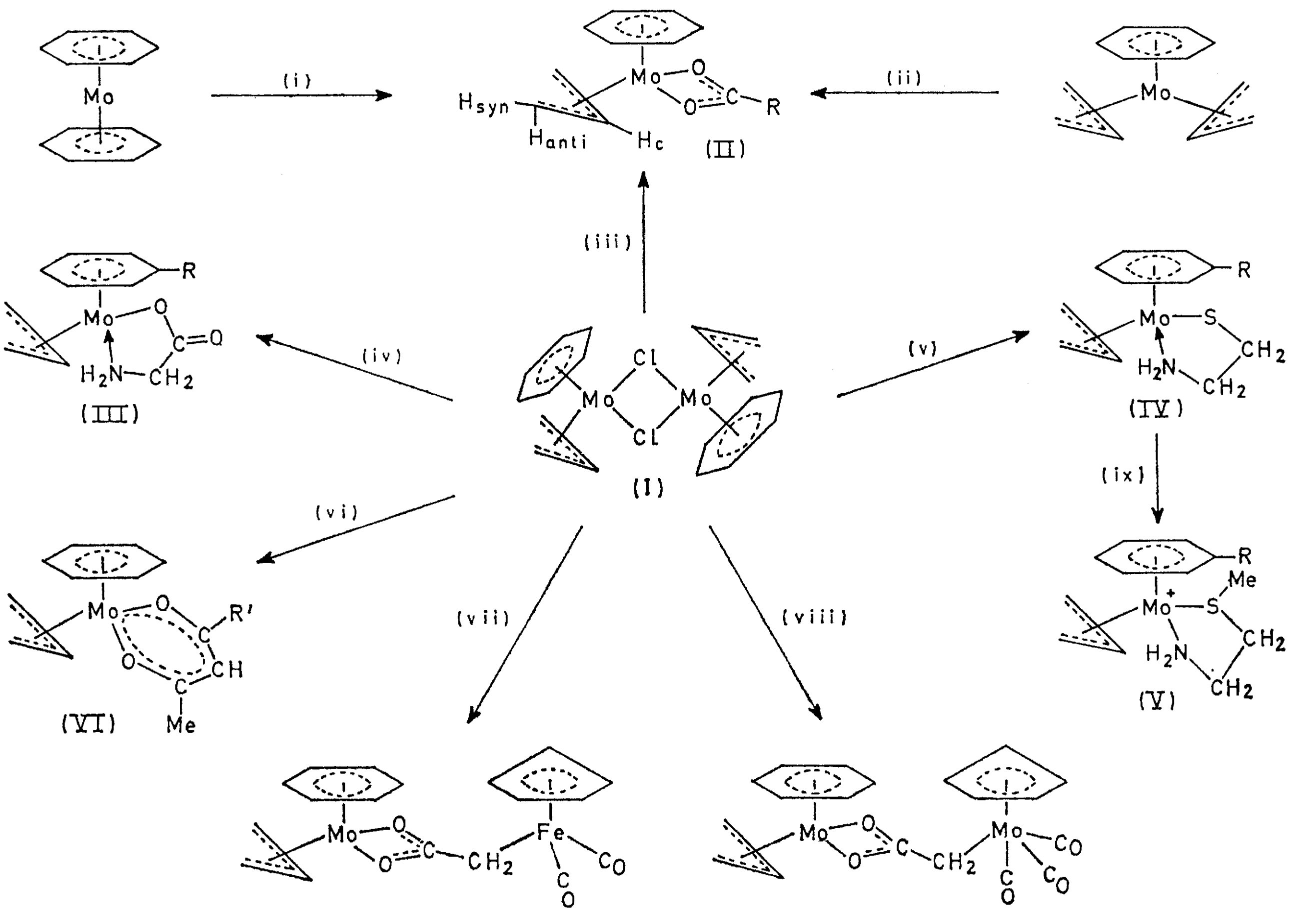
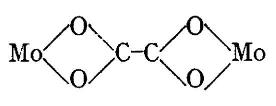
[3] L. Lawton and R. Mason, *J. Amer. Chem. Soc.*, 1965, **87**, 92.

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

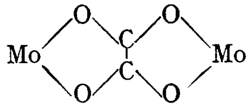


SCHEME (i), $C_3H_5CO_2Me$; (ii), RCO_2H, R = H, Me, or Ph; (iii), RCO_2Na, R = H, Me, Ph, *p*-$C_6H_4CO[Fe(CO)_2(\pi\text{-}C_5H_5)]$, *p*-$C_6H_4CO_2Me$, and CH_2CO_2Et; (iv), $NH_2CH_2CO_2K$, R = H or Me; (v), $KS[CH_2]_2NH_2$, R = H or Me; (vi), K(MeCOCH-COCR), R = Me or OEt; (vii), $(\pi\text{-}C_5H_5)Fe(CO)_2CH_2CO_2K$; (viii), $(\pi\text{-}C_5H_5)Mo(CO)_3CH_2CO_2K$; (ix), $MeI\text{-}PF_6^-$, R = H

group. These are the *cis*- and *trans*-isomers of the compound where the μ-oxalato-group is bonded either as shown in (A) or in (B):



(A)



(B)

The ^1H n.m.r. data suggests the presence of only one major isomer (80—90%) but does not permit distinction between the alternatives. The occurrence of a strong band at 1640 cm^{-1} is atypical of the terminal carboxylato-compounds (II) and this might suggest that the isomer has structure (B). In fact, the structure (B) has been proposed for other binuclear μ-oxalato-complexes, *e.g.* $Et_2Au(C_2O_4)AuEt_2$ [5] and $Bu_3PClPd(C_2O_4)PdClPBu_3$.[6] In the absence of further evidence structure (B) seems the most likely for the molybdenum analogue.

(b) *Amino-acid derivatives*. Treatment of the dimers $[RC_6H_5Mo(\pi\text{-}C_3H_5)Cl]_2$ (I; R = H or Me) with potassium glycinate gives deep pink, air-stable compounds of stoicheiometry $RC_6H_5Mo(\pi\text{-}C_3H_5)NH_2CH_2CO_2$ (III; R = H or Me). They are not sufficiently soluble for determination of the ^1H n.m.r. spectra although they dissolve slightly in chloroform, dimethyl sulphoxide, and ethanol. With dilute acids they are decomposed liberating propene. The i.r. spectra show bands assignable to a $\pi\text{-}C_3H_5$ system, $\pi\text{-}C_6H_6$, and to a co-ordinated glycinato-ligand,[7, 8] see the Table. The mass spectrum of (III; R = H) shows a parent ion peak corresponding to a monomeric formulation, at $M^+/e = 291$. We therefore propose the structures for the compounds (III; R = H or Me) which are given in the Scheme.

The dimers (I; R = H or Me) react with alkaline solutions of mercaptoethanolamine giving air-stable, purple crystals of stoicheiometry $RC_6H_5Mo(\pi\text{-}C_3H_5)\text{-}NH_2[CH_2]_2S$ (IV; R = H or Me). These are also of too low solubility for determination of their ^1H n.m.r. spectra. They dissolve only very slightly in chloroform

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[5] C. S. Gibson and W. T. Weller, *J. Chem. Soc.*, 1941, 102.

[6] J. Chatt and F. G. A. Mann, *J. Chem. Soc.*, 1938, 1949.

[7] K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Amer. Chem. Soc.*, 1961, **83**, 4528.

[8] E. S. Gore and M. L. H. Green, *J. Chem. Soc.* (*A*), 1970, 2315.

or tetrahydrofuran, and slightly in ethanol. They are decomposed by hydrochloric acid liberating propene. The i.r. spectra show bands consistent with the presence of the groups C_6H_6, π-C_3H_5, and $NH_2[CH_2]_2S$; structures similar to those of the glycinato-derivatives (III) are proposed.

Treatment of the complex (IV; R = H) with methyl iodide, followed by isolation of the cationic product as the hexafluorophosphate salt, gives the compound $[C_6H_6Mo(\pi\text{-}C_3H_5)MeS\{CH_2\}_2NH_2]^+PF_6^-$ (V). This is soluble in dimethyl sulphoxide and the ^1H n.m.r. spectrum is consistent with the above formulation but is very complex due to both the coincidence of chemical shift and the non-equivalence of the π-allyl hydrogens. The i.r. spectrum shows bands assignable to the groups C_6H_6, π-C_3H_5, and NH_2. An alternative formulation for the compound (V), for example, containing the group $HS(CH_2)_2NHMe$, is consistent with the above evidence, since S–H stretching frequencies are weak and non-observance is not diagnostic. However, since the N–H stretching frequencies are similar to those in the parent compound (IV; R = H) and since methylation of the sulphur has been shown in reactions of related compounds [9] we prefer the structure given in the Scheme.

(c) *Reaction with β-diketones.* The dimer (I; R = H) reacts readily with ethanol solution of potassium acetylacetonate giving a dark red compound of stoicheiometry $C_6H_6Mo(\pi\text{-}C_3H_5)MeCO\cdot CH\cdot COMe$ (VI). This is soluble in the common organic solvents and solutions are slowly decomposed in air (days). The data given in the Table strongly suggest the proposed structure given in the Scheme. The ethylacetoacetato-derivative $C_6H_6Mo(\pi\text{-}C_3H_5)MeCO\cdot CH{:}CO(OEt)$ is prepared in a similar manner to that of the compound (VI) and the data suggests it has the analogous structure.

When the dimer (I; R = H) is treated with diethyl malonate in the presence of base then the purple crystals obtained are not analogous to the above compound (VI). The stoicheiometry and spectral data correspond to the formulation as a carboxylato-derivative $C_6H_6Mo(\pi\text{-}C_3H_5)O_2CCH_2CO_2Et$ (II; R = CH_2CO_2Et). The compound is soluble in most common organic solvents. Presumably the diethyl malonate is hydrolysed giving the anion $EtO_2CCH_2CO_2^-$ which then reacts with the dimer (I; R = H).

In conclusion, the above studies show that the (arene)-$Mo(\pi\text{-}C_3H_5)$ system is both stable to decomposition under a variety of conditions, except to acid treatment, and that it can bond to a variety of common oxygen, nitrogen, and sulphur ligands.

EXPERIMENTAL

All preparations and purification were carried out in the absence of oxygen. Where required, solvents were dried by refluxing over and distillation from calcium hydride. Light petroleum is AnalaR, 30—40°. ^1H N.m.r. spectra were determined on a JEOL 60 MHz instrument or on a Perkin-Elmer 100 MHz instrument. I.r. spectra were measured on mulls using a Perkin-Elmer 457 instrument calibrated with polystyrene. Low resolution mass spectra were determined using an A.E.I. MS-9 spectrometer. Molecular weights were determined in benzene using a Mecrolab osmometer. The compounds $[RC_6H_5Mo(\pi\text{-}C_3H_5)Cl]_2$ and $C_6H_6Mo(\pi\text{-}C_3H_5)_2$ were prepared as previously described.[1,10]

Acetato(π-allyl)benzenemolybdenum.—Method A. Bis(π-allyl)benzenemolybdenum (0·25 g, 1·0 mmol) in benzene (20 ml) was treated with glacial acetic acid (0·06 ml, 1·0 mmol). The initially orange solution steadily changed to purple and a gas was evolved. After 1 h the solvent was removed under reduced pressure giving a purple solid which was extracted with light petroleum (15 ml). The extract was filtered and the purple filtrate was cooled slowly to −10° giving long needle crystals, *ca.* 90%.

Method B. Bisbenzenemolybdenum (2·5 g) in benzene (200 ml) was treated with allyl acetate (5 ml) and the solution was kept at room temperature for 3 days. The green solution slowly deposited purple crystals. The solvent was removed under reduced pressure and the residue was extracted with light petroleum (400 ml) and the solution was filtered. The filtrate was concentrated (200 ml) and then cooled to −50° giving purple crystals which were collected and dried in vacuum, *ca.* 65%.

Method C. Sodium acetate (0·16 g, 2·0 mmol) was added to a suspension of the dimer $[C_6H_6Mo(\pi\text{-}C_3H_5)Cl]_2$ (0·5 g, 1·0 mmol) in 95% ethanol (20 ml) and the mixture was stirred at 50° for 1 h. The solution became purple and a white solid precipitated. The mixture was cooled to room temperature, filtered, and solvent was removed from the filtrate under reduced pressure leaving a purple residue. This was extracted with light petroleum (10 ml), the extract was filtered, concentrated, and cooled to −10° giving purple crystals which were separated and dried under vacuum, *ca.* 95%.

Benzoato(π-allyl)benzenemolybdenum.—Method A. Bis-(π-allyl)benzenemolybdenum (0·25 g, 1·0 mmol) in benzene (10 ml) was treated with benzoic acid (0·12 g, 1·0 mmol) in benzene (10 ml). After stirring for 90 min the orange solution had become dark red-yellow. The solvent was removed under reduced pressure giving a brown solid which was extracted with light petroleum (15 ml). The extract was filtered and the yellow-brown filtrate was cooled slowly to −30° giving golden-brown needles which were collected and dried under vacuum. A second recrystallisation, as above, gave the pure *compound*, *ca.* 85%.

Method B. Sodium benzoate (0·14 g, 1·0 mmol) was added to a suspension of the dimer $[C_6H_6Mo(\pi\text{-}C_3H_5)Cl]_2$ (0·25 g, 0·5 mmol) in 95% ethanol and the mixture was stirred at 50° for 2 h, giving a red-brown solution. The product was isolated as described in Method A, *ca.* 74%.

Formato(π-allyl)benzenemolybdenum.—Method A. Bis(π-allyl)benzenemolybdenum (0·25 g, 1·0 mmol) in benzene (5 ml) was treated with formic acid (0·04 ml, 1·0 mmol). The orange solution immediately changed to purple and gas was evolved. The solvent was removed under reduced pressure leaving a purple solid which was extracted with hot light petroleum (60—80°). The hot extract was filtered and the purple filtrate was cooled slowly to −30° giving long needle crystals which were separated and dried under vacuum. A repeated recrystallisation, as above, gave the pure *compound*, *ca.* 72%.

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[9] R. V. G. Ewens and C. S. Gibson, *J. Chem. Soc.*, 1949, 431.

[10] M. L. H. Green and W. E. Silverthorn, *J.C.S. Dalton*, 1973, 301.

Method B. Sodium formate (0·15 g, 2·0 mmol) was added to a suspension of the dimer $[C_6H_6Mo(\pi\text{-}C_3H_5)Cl]_2$ (0·5 g, 1·0 mmol) in 95% ethanol (20 ml) and the mixture was stirred at 50° for 30 min. The solution became purple and a white solid deposited and the mixture was filtered. The solvent was removed from the purple filtrate under reduced pressure giving an oily solid which was dried for 1 h and then extracted with hot light petroleum (b.p. 60—80°). The pure product was isolated from the extract in the manner described above in Method A, *ca.* 95%.

p-*Carboxymethylbenzoato*(π-*allyl*)*benzenemolybdenum*.—Potassium *p*-carboxymethylbenzoate (0·22 g, 1·0 mol) was added to a suspension of the dimer (I; R = H) (0·25 g, 0·5 mmol) in 95% ethanol (20 ml) and the mixture was stirred at 55° for 1 h. The solution became deep red. The solvent was removed under reduced pressure and the deep pink residue was extracted with hot light petroleum (b.p. 100—120°, 10 ml). The extract was filtered and cooled giving dark red crystals which were collected, washed with light petroleum, and dried in vacuum, *ca.* 90%.

[*Dicarbonyl*(π-*cyclopentadienyl*)*iron*]*acetato*(π-*allyl*)*benzenemolybdenum*.—A suspension of the dimer (I; R = H) (0·25 g, 1·0 mmol) in 95% ethanol (20 ml) was treated with [dicarbonyl(π-cyclopentadienyl)iron]acetic acid [2] (0·23 g, 1·0 mmol) and potassium hydroxide (0·05 g, 1·0 mmol) in water (1 ml) and the mixture was stirred for 1 h at 60 °C. The solution became deep red and red crystals were deposited. The solvent was removed under reduced pressure and the red residue was extracted with benzene (10 ml). The extract was filtered and the deep red filtrate was treated with light petroleum (b.p. 100—120°, 5 ml). Slow removal of the solvent under reduced pressure precipitated small red crystals which were collected and washed with light petroleum and dried in vacuum, *ca.* 65%.

p-[*Dicarbonyl*(π-*cyclopentadienyl*)*iron*]*oxomethylbenzenecarboxylato*](π-*allyl*)*benzenemolybdenum*.—A suspension of the dimer (I; R = H) (0·25 g, 1·0 mmol) in 95% ethanol (25 ml) was treated with *p*-[dicarbonyl(π-cyclopentadienyl)-iron]oxomethylbenzenecarboxylic acid [11] (0·32 g, 1·0 mmol) and potassium hydroxide (0·05 g, 1·0 mmol) in water (1 ml) and the mixture was stirred for 30 min at 60°. The solution became deep red and red crystals appeared. The solvent was removed under reduced pressure and the residue was extracted with benzene (15 ml) and filtered. Petroleum ether was added to the filtrate and concentration of the solution precipitated dark red crystals which were separated, washed with petroleum, and dried in vacuum, *ca.* 85%.

[*Tricarbonyl*(π-*cyclopentadienyl*)*molybdenum*]*acetato*(π-*allyl*)*benzenemolybdenum*.—This was prepared from the dimer (I; R = H) (0·25 g) and the acid $(\pi\text{-}C_5H_5)Mo(CO)_3\text{-}CH_2CO_2H$ [2] (0·30 g) in aqueous potassium hydroxide, as described above for the iron analogue. Recrystallisation was from light petroleum giving red needle crystals, *ca.* 70%.

(*Methoxycarbonyl*)*acetato*(π-*allyl*)*benzenemolybdenum*.—The dimer (I; R = H) (0·25 g) was treated with ethanol (25 ml), ethyl malonate (0·81 ml), and potassium hydroxide (0·05 g) and the mixture was stirred at 80° for 30 min. The product was isolated as described above. Recrystallisation was from light petroleum (b.p. 60—80°), *ca.* 95%.

μ-*Oxalato-bis*[(π-*allyl*)*benzenemolybdenum*].—*Method A*. Oxalic acid dihydrate (0·07 g, 0·5 mmol) in 95% ethanol was added dropwise to bis(π-allyl)benzenemolybdenum (0·25 g, 1·0 mmol) in 95% ethanol (10 ml). The red crystals which precipitated were recrystallised from benzene-light petroleum (b.p. 100—120°) twice, *ca.* 65%

Method B. A suspension of the dimer $[C_6H_6Mo(\pi\text{-}C_3H_5)\text{-}Cl]_2$ (0·5 mmol) in ethanol (95%, 20 ml) was treated with sodium oxalate (1·0 mmol) and the mixture was stirred at 50° for 2 h. The product was isolated as described in Method A, *ca.* 65%.

Acetylacetonato(π-*allyl*)*benzenemolybdenum*.—A suspension of the dimer $[C_6H_6Mo(\pi\text{-}C_3H_5)Cl]_2$ in ethanol (95%, 25 ml) was treated with acetylacetone (0·10 ml, 1·0 mmol) and potassium hydroxide (0·05 g) in water (1 ml), and the mixture was stirred at 80° for 30 min. The product was isolated as described for the carboxylato-derivatives, recrystallisation was from hot light petroleum (b.p. 100—120°) (twice), *ca.* 95%.

The ethylacetoacetonato-derivative $C_6H_6Mo(\pi\text{-}C_3H_5)\text{-}MeCO{\cdot}CH{\cdot}CO(OEt)$ was similarly prepared from ethylacetate. Recrystallisation was from light petroleum, *ca.* 80%.

(2-*Mercaptoethylamine*)(π-*allyl*)*benzenemolybdenum*.— A suspension of the dimer (I; R = H) in ethanol (95%, 25 ml) was treated with 2-mercaptoethylamine hydrochloride (0·12 g) and potassium hydroxide (0·11 g) and the mixture was stirred at 70° for 1 h. The solvent was removed under reduced pressure giving a brown, microcrystalline residue which was washed with water (2 × 5 ml) and then extracted with hot ethanol (95%, 20 ml). The extract was filtered and water was added to the deep red filtrate. Reduction of the volume of the mixture under reduced pressure precipitated red-brown needles which were collected and recrystallised twice more and finally dried in vacuum, *ca.* 72%.

The toluene analogue $MeC_6H_5Mo(\pi\text{-}C_3H_5)S[CH_2]_2NH_2$ was similarly prepared, starting with the dimer (I; R = Me), *ca.* 65%.

(2-*Thiabutylamine*)(π-*allyl*)*benzenemolybdenum Hexafluorophosphate*.—A solution of the compound $C_6H_6Mo(\pi\text{-}C_3H_5)S\text{-}[CH_2]_2NH_2$ (0·2 g) in ethanol was treated with methyl iodide and the mixture was allowed to stand for 30 min at room temperature. A saturated aqueous solution of ammonium hexafluorophosphate was added giving a red precipitate. This was collected, washed with water, and then extracted with acetone (15 ml). The extract was filtered and water (8 ml) was added to the filtrate. The volume of the mixture was slowly reduced under reduced pressure giving small dark red crystals. These were recrystallised twice more and finally dried in vacuum, *ca.* 85%.

Glycinato(π-*allyl*)*benzenemolybdenum*.—A suspension of the dimer (I; R = H) in ethanol (95%, 25 ml) was treated with glycine and potassium hydroxide in the same proportions used in the preparation of the terminal carboxylato-derivatives and the product was isolated in the same way. Recrystallisation was from ethanol-light petroleum (b.p. 100—120°), *ca.* 55%. The analogue $MeC_6H_5Mo(\pi\text{-}C_3H_5)\text{-}NH_2CH_2CO_2$ was prepared in a similar manner starting from the dimer (I; R = Me).

Reaction between Bis(π-*allyl*)*benzenemolybdenum and an Excess of Acetic Acid*.—Bis(π-allyl)benzenemolybdenum (0·25 g, 1·0 mmol) in benzene (20 ml) was treated with excess glacial acetic acid (2 ml). An immediate gas evolution accompanied a change of colour from orange to purple and after 1 min green crystals separated. The gas evolved was shown to be propene by g.l.c. analysis. Analysis and

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[11] J. D. Duncan, D.Phil. Thesis, Oxford, 1968.

i.r. spectra showed the green product to be the previously described dimer $Mo_2(MeCO_2)_4$, *ca.* 90%. The same product was similarly obtained from bis(π-allyl)toluenemolybdenum. Also, when trifluoroacetic acid was used in place of acetic acid the analogue $Mo_2(CF_3CO_2)_4$ was similarly obtained, *ca.* 90% (Found: C, 22·8; H, 2·9. Calc. for $C_8H_{12}Mo_2O_8$: C, 22·4; H, 2·8%. Found: C, 15·3; H, 0·3; Calc. for $C_8F_{12}Mo_2O_8$: C, 14·9; H, 0·0%).

Reaction between Acetato(π-allyl)benzenemolybdenum and Acetic Acid.—Acetato(π-allyl)benzenemolybdenum (0·27 g, 1·0 mmol) in benzene (10 ml) was treated with an excess of acetic acid (10 ml). As observed in the above reaction, green crystals rapidly separated from the mixture. These were identified as the dimer $Mo_2(MeCO_2)_4$, *ca.* 90%.

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