

Carbonyl- π -cyclopentadienyl Complexes of Molybdenum

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A number of derivatives of the halogenocarbonyl- π -cyclopentacarbonylmolybdenum complexes $C_5H_5Mo(CO)_3X$ ($X = Cl$ or I) has been prepared. Three types of compound have been isolated: (i) those containing the substituted cation $[C_5H_5Mo(CO)_2L_2]^+$, where $L = PEt_3$ and PPh_3 or $L_2 = 1,2$ -bis(diphenylphosphino)ethane (Diphos) and *o*-phenylenebisdimethylarsine (Diars); (ii) the monosubstituted halides $C_5H_5Mo(CO)_2LCl$, where $L = PPh_3$, $AsPh_3$, $SbPh_3$, and $\frac{1}{2}$ Diphos, and $C_5H_5Mo(CO)_2LI$, where $L = PEt_3$, $P(cyclohexyl)_3$, PPh_3 , $P(OPh)_3$, $AsMePh_2$, $AsPh_3$, and $SbPh_3$; (iii) the disubstituted halides $C_5H_5Mo(CO)L_2Cl$, where $L = PEt_3$, PPh_3 , $AsPh_3$, and $SbPh_3$ and $L_2 = Diphos$, and $C_5H_5Mo(CO)L_2I$, where $L = PEt_3$, $P(OPh)_3$, $AsMePh_2$, and $SbPh_3$, and $L_2 = Diphos$ and Diars. The physical properties of these complexes are presented and discussed.

PREVIOUS investigations have illustrated that the halogenocarbonyl- π -cyclopentadienyl derivatives of molybdenum and tungsten react with a variety of ligands to yield derivatives of two types: those in which carbon monoxide only is displaced, *e.g.*, $C_5H_5Mo(CO)_2(PhNC)I$,¹ $C_5H_5Mo(PhNC)_3Cl$,¹ $C_5H_5Mo(CO)_2[P(NMe_2)_3]I$,² $C_5H_5W(CO)_2PEt_3Cl$,³ and $C_5H_5W(CO)_2(PPh_3)Cl$,³ and those in which the halide ion is displaced to yield an ionic product, *e.g.*, $[C_5H_5Mo(CO)_3(NH_3)]$,⁴ $[C_5H_5W(CO)_3(N_2H_4)]Cl$,⁴ and $[C_5H_5W(CO)_2(PEt_3)_2]Cl$.³ However, no extensive and systematic study of such reactions has been reported. In this Paper the results of an investigation of the reactions of the compounds $C_5H_5Mo(CO)_3Cl$ and $C_5H_5Mo(CO)_3I$ with a wide range of ligands are discussed.

Ionic Compounds.—Triethylphosphine and 1,2-bis(diphenylphosphino)ethane (Diphos) react in solution with the compound $C_5H_5Mo(CO)_3Cl$ at room temperature, to yield the ionic compounds $[C_5H_5Mo(CO)_2(PEt_3)_2]Cl$ and $[C_5H_5Mo(CO)_2(Diphos)]Cl$, respectively. In similar conditions, reaction with triphenylphosphine did not occur. Under ultraviolet irradiation, however, carbon monoxide was evolved to yield the neutral substituted compounds $C_5H_5Mo(CO)_2(PPh_3)Cl$ and $C_5H_5Mo(CO)(PPh_3)_2Cl$. The cationic species containing triphenylphosphine could be prepared provided the reaction was carried out in the presence of aluminium trichloride, when a yellow crystalline derivative $[C_5H_5Mo(CO)_2(PPh_3)_2]AlCl_4$ separated. Reaction of the iodide $C_5H_5Mo(CO)_3I$ with these ligands produced only neutral species. The ligand *o*-phenylenebisdimethylarsine (Diars) reacted with the iodide, however, under ultraviolet irradiation to yield the salt $[C_5H_5Mo(CO)_2(Diars)]I$. It was found to be most convenient to isolate the cations in the form of their crystalline perchlorates by metathetical reaction with lithium perchlorate in acetone. These complexes (Table 1) can be considered to be disubstituted derivatives of the carbonyl cation $[C_5H_5Mo(CO)_4]^+$. This cation can be assumed to have, like the complex $C_5H_5V(CO)_4$, a structure in which the carbonyl groups are disposed in a local C_{4v} symmetry. Hence, it is possible that cations of the type $[C_5H_5Mo(CO)_2L_2]^+$, where L is a unidentate ligand,

could exist in two isomeric forms, in which "*cis*" and "*trans*" carbonyl groups have been displaced. The infrared spectra of the chelate-substituted compounds in the C—O stretching region contain two bands of approximately equal intensity, while in the corresponding spectra of the bis-unidentate compounds, the higher-frequency band is of markedly diminished intensity. This difference may result from differing positions of substitution.

Monosubstituted Compounds.—Equimolar quantities of the compound $C_5H_5Mo(CO)_3Cl$ and the ligands PPh_3 , $AsPh_3$, and $SbPh_3$ react under ultraviolet irradiation to yield the monosubstituted derivatives of the type $C_5H_5Mo(CO)_2LCl$. Similar compounds are formed on reaction of the iodide with the ligands PEt_3 , $P(cyclohexyl)_3$, $P(OPh)_3$, $AsMePh_2$, $AsPh_3$, and $SbPh_3$. Reaction of the ligands $P(C_6F_5)_3$ with $C_5H_5Mo(CO)_3Cl$ and $C_5H_5Mo(CO)_3I$ and pyridine with $C_5H_5Mo(CO)_3I$ did not occur.

With the exception of that of the compound $C_5H_5Mo(CO)_2PPh_3I$, the infrared spectra of the compounds in the C—O stretching region in the solid state and in solution contained two strong bands. The spectrum of the former, which shows bands at 1957, 1874, and 1853 cm^{-1} in the solid state, suggests the existence of two isomers although only two bands are observed in chloroform solution. The general outline of the solution spectrum differs from that of the other compounds, however, and it appears that the expected four bands are not resolved in this solvent. Further, the proton magnetic resonance spectrum of the compound in deuteriochloroform shows singlet and doublet resonances resulting from the cyclopentadienyl protons. This supports strongly the existence of two isomers in solution, one giving a singlet at 4.58 τ and the other giving the doublet at 4.84 τ ($J = 2.1$ c./sec.). The formation of the doublet results presumably from coupling with the spin of the ^{31}P nucleus. A similar observation was made by King² in the spectrum of the compound $C_5H_5Mo(CO)_2[P(NMe_2)_3]I$. The proton resonance spectra of all the other monosubstituted compounds prepared contained only one peak (Table 1) confirming that they contain only one isomer.

² E. O. Fischer and E. Moser, *J. Organometallic Chem.*, 1966, 5, 63.

⁴ E. O. Fischer and E. Moser, *J. Organometallic Chem.*, 1964, 2, 230.

¹ K. K. Joshi, P. L. Pauson, and W. H. Stubbs, *J. Organometallic Chem.*, 1963, 1, 53.

² R. B. King, *Inorg. Chem.*, 1963, 2, 936.

TABLE I
 Physical properties of complexes

No.	Compound *	Colour	M. p.†	$\Lambda_M(\Omega^{-1} \text{ cm.}^2)$	Conc. ($\times 10^{-3} M$)
I	$C_6H_5Mo(CO)(PET_3)_2Cl$	Brown	153—155°	0.34	1.8
II	$C_6H_5Mo(CO)_2(PPh_3)Cl$	Orange	170d	0.16	0.9
III	$C_6H_5Mo(CO)_2(PPh_3)_2Cl$	Orange	188d	0.25	1.3
IV	$C_6H_5Mo(CO)_2(AsPh_3)Cl$	Orange	172d	0.21	1.7
V	$C_6H_5Mo(CO)_2(AsPh_3)_2Cl$	Orange	141d	0.33	1.5
VI	$C_6H_5Mo(CO)_2(SbPh_3)Cl$	Orange	173d	0.18	1.5
VII	$C_6H_5Mo(CO)_2(SbPh_3)_2Cl$	Orange	160d	0.26	1.1
VIII	$[C_6H_5Mo(CO)_2Cl]_2(Diphos)$	Orange	170d	0.17	2.3
IX	$C_6H_5Mo(CO)(Diphos)Cl$	Orange	235d	0.12	1.5
X	$C_6H_5Mo(CO)_2(PET_3)I$	Red	67—69	0.12	5.5
XI	$C_6H_5Mo(CO)(PET_3)_2I$	Red-brown	134—137	0.06	3.2
XII	$C_6H_5Mo(CO)_2[P(\text{cyclohexyl})_3]I$	Red	178—180d	0.60	1.1
XIII	$C_6H_5Mo(CO)_2(PPh_3)I$	Red	175—177d	0.60	1.2
XIV	$C_6H_5Mo(CO)_2[P(OPh)_3]I$	Red	154—156d	0.08	1.6
XV	$C_6H_5Mo(CO)[P(OPh)_3]_2I$	Orange	114—116	0.34	1.4
XVI	$C_6H_5Mo(CO)_2(AsMePh_2)I$	Red	138—140	0.15	1.9
XVII	$C_6H_5Mo(CO)(AsMePh_2)_2I$	Red	—	0.63	1.1
XVIII	$C_6H_5Mo(CO)_2(AsPh_3)I$	Red	158d	0.40	1.5
XIX	$C_6H_5Mo(CO)_2(SbPh_3)I$	Red	163d	0.55	1.5
XX	$C_6H_5Mo(CO)(SbPh_3)_2I$	Red	145d	0.53	1.1
XXI	$C_6H_5Mo(CO)(Diphos)I$	Red	156—158	0.18	1.5
XXII	$C_6H_5Mo(CO)(Diars)I$	Red	126—128	0.22	2.2
XXIII	$[C_6H_5Mo(CO)_2(PET_3)_2]ClO_4$	Yellow	—	180 ^a	0.8
XXIV	$[C_6H_5Mo(CO)_2(PPh_3)_2]ClO_4$	Yellow	—	172 ^a	0.7
XXV	$[C_6H_5Mo(CO)_2(Diphos)]ClO_4$	Yellow	—	193 ^a	1.6
XXVI	$[C_6H_5Mo(CO)_2(Diars)]I$	Yellow	—	109 ^a	1.8

No.	M^\ddagger		C—O str. frequencies (I.R., cm.^{-1}) §	Mo—Cl str. frequency (I.R., cm.^{-1})	C_6H_5 proton resonance ¶ (p.p.m.)	Visible absn. max. ($m\mu$)
	Found	Calc.				
I	448	461	1778	247	4.90	407
II	515	515	1976, 1887	275	4.44	476
III	735	749	1795	267	5.09	455
IV	551	559	1975, 1886	273	4.38	479
V	809	837	1791	266	4.95	463
VI	607	606	1974, 1884	276	4.31	484
VII	915	931	1796	267	4.61	438
VIII	877	903	1967, 1880	275	—	477
IX	604	623	1845	261	5.37	479
X	448	462	1963, 1877 ^b	—	—	498
XI	541	552	1798 ^b	—	4.31	—
XII	613	624	1956, 1874	—	4.52	—
XIII	583	606	1967, 1888	—	4.58, 4.84	470
XIV	636	654	1992, 1918	—	—	480
XV	909	936	1873	—	5.25	—
XVI	576	588	1968, 1882 ^b	—	4.55	498
XVII	776	804	1807 ^b	—	—	—
XVIII	638	650	1966, 1883	—	4.40	475
XIX	682	697	1964, 1880	—	4.41	486
XX	1037	1022	1812 ^b	—	4.75	—
XXI	706	714	1852	—	v. broad	—
XXII	590	602	1844	—	—	—
XXIII	—	—	1958ms, 1877	—	—	—
XXIV	—	—	1979ms, 1896	—	—	—
XXV	—	—	1979ms, 1914	—	—	—
XXVI	—	—	1978, 1912	—	—	—

* All are diamagnetic in the solid state at 20°. † d = decomposes. ‡ In benzene osmometrically. § In $CHCl_3$; bands are strong unless stated otherwise. || In CH_2Cl_2 ($\epsilon \sim 5-8 \times 10^3$). ¶ τ scale in $CDCl_3$.

^a In acetone. ^b In CCl_4 .

Disubstituted Compounds.—Neutral disubstituted derivatives of the compound $C_6H_5Mo(CO)_3Cl$ resulted from reaction of excess of the ligands PPh_3 , $AsPh_3$, and $SbPh_3$ under prolonged irradiation with ultraviolet light. Similarly, reaction of the ligands $PET_3 \cdot P(OPh)_3$, $AsMePh_2$, and $SbPh_3$ with the corresponding iodide again yielded disubstituted products. However, in the same experimental conditions, the ligands $P(\text{cyclohexyl})_3$, PPh_3 , and $AsPh_3$ failed to displace more than one carbonyl group. Presumably, several factors will determine whether or not a particular ligand will form a

disubstituted product. However, of these, it appears that steric features may play a dominant role. For example, the main difference between the behaviour of the ligands $AsPh_3$ and $AsMePh_2$ (only the latter forms the disubstituted iodide) is likely to be steric in nature.

The chelate ligands *o*-phenylenebisdimethylarsine and 1,2-bis(diphenylphosphino)ethane react with the compound $C_6H_5Mo(CO)_3I$ to form the product $C_6H_5Mo(CO)(Diars)I$ and $C_6H_5Mo(CO)(Diphos)I$, respectively. The reactions proceed slowly and irradiation for periods in excess of 40 hr. are required. Similarly, the chloride

derivative $C_5H_5Mo(CO)(Diphos)Cl$ was prepared. Previously,⁵ reaction of these chelate ligands with the manganese complex $C_5H_5Mn(CO)_3$ was shown to lead also to derivatives in which the donor atom co-ordinated independently to separate metal atoms. Similarly, the compound $[C_5H_5Mo(CO)_2Cl]_2(Diphos)$ was isolated and infrared spectroscopic evidence obtained for the formation of the analogous iodide.

Differences in the infrared spectra of related compounds containing uni- and bi-dentate ligands may be significant: *e.g.*, $C_5H_5Mo(CO)(PPh_3)_2Cl$, 1795 cm^{-1} ; $C_5H_5Mo(CO)(Diphos)Cl$, 1845 cm^{-1} . This behaviour

^{31}P nucleus since coupling constants only of the order of 1–2 c./sec. are expected⁶ [and observed in the spectra of the complexes $C_5H_5Mo(CO)_2LI$; $L = PPh_3$ and $P(NMe_2)_3$]. Further, a study of the temperature-dependence of the proton resonance of the compound $C_5H_5Mo(CO)(PEt_3)_2I$ showed a sharpening of the resonance with increase in temperature: half-band widths at 30, 40, and 50° are 34, 26, and 18 c./sec., respectively. This observation appears to eliminate the possibility of coupling as the cause of the broadening, since coupling constants should be approximately temperature-independent. We presume, consequently,

TABLE 2
Preparation of complexes

No.	Wts. of reactants (g.)		Solvent	Irradiation time (hr.)	Wt. of product (g.)
	$C_5H_5Mo(CO)_3X$	Ligand			
I	0.35	0.60	Benzene	70	0.37
II	0.56	0.52	Benzene-cyclohexane	30	0.85
III	0.47 *	0.93	Benzene-cyclohexane †	30	0.40
IV	0.57	0.62	Benzene-cyclohexane	30	0.90
V	0.30 *	0.60	Benzene-cyclohexane †	90	0.30
VI	0.40	0.53	Benzene-cyclohexane	40	0.70
VII	0.56 *	0.70	Benzene-cyclohexane †	100	0.40
VIII	0.42	0.60	Benzene	75	0.25
IX	0.42	0.60	Benzene	75	0.30
X	0.49	0.15	Benzene-cyclohexane	25	0.32
XI	0.40	0.49	Benzene	72	0.34
XII	0.30	0.23	Benzene-cyclohexane	50	0.40
XIII	0.60	0.42	Benzene-cyclohexane	30	0.80
XIV	0.32	0.29	Benzene-cyclohexane	30	0.45
XV	0.30	0.90	Benzene	100	0.35
XVI	0.75	0.47	Benzene-cyclohexane	30	0.90
XVII	0.52	1.35	Benzene	96	0.30
XVIII	0.37	0.31	Benzene-cyclohexane	30	0.50
XIX	0.60	0.57	Benzene-cyclohexane	60	0.85
XX	0.50	1.0	Benzene-cyclohexane	100	0.35
XXI	0.40	0.44	Benzene	90	0.50
XXII	0.35	0.42	Benzene (40 ml.)	60	0.30
XXVI	0.57	0.43	Benzene	30	0.45

* Monosubstituted compounds $C_5H_5Mo(CO)_2LX$. † Mixture chosen so that *ca.* 50% of chloride dissolves.

contrasts with that found in the spectra of the compounds $C_5H_5Mn(CO)(Diphos)$ and $C_5H_5Mn(CO)(PPh_3)_2$, where the bands occur in very similar positions (at 1827 and 1818 cm^{-1} , respectively) and may reflect differing positions of substitution in the former compounds.

N.m.r. Spectra.—As indicated earlier, the proton magnetic resonance spectra of all the mono-substituted compounds studied, except for $C_5H_5Mo(CO)_2(PPh_3)I$, contained one sharp resonance peak due to cyclopentadienyl protons. Similarly, the spectra of the compounds $C_5H_5Mo(CO)(AsPh_3)_2Cl$, $C_5H_5Mo(CO)(SbPh_3)_2Cl$, $C_5H_5Mo(CO)[P(OPh)_3]_2I$, and $C_5H_5Mo(CO)(SbPh_3)_2I$, in deuteriochloroform contained one peak in the cyclopentadienyl proton region, the half-band width being of the order of 1–3 c./sec. The spectra of the complexes $C_5H_5Mo(CO)(PEt_3)_2Cl$, $C_5H_5Mo(CO)(PPh_3)_2Cl$, $C_5H_5Mo(CO)(Diphos)Cl$, $C_5H_5Mo(CO)(PEt_3)_2I$, and $C_5H_5Mo(CO)(Diphos)I$, however, contain very broad resonance peaks (half-band widths *ca.* 30 c./sec.). It is most unlikely that this broadening results from spin-spin coupling with the

that the observed broadening results from restricted rotation of the cyclopentadienyl ring in these disubstituted products, which, in turn, results from steric interactions with the substituent ligands.

EXPERIMENTAL

General Methods of Preparation of Complexes.—All were prepared in an evacuated Pyrex tube with the same volume of solution (60 ml.). The solvents were benzene or benzene-cyclohexane (1 : 1), unless stated otherwise. Most reactions were carried out under ultraviolet radiation (60 w). Where possible, the relevant details of amounts of material used and reaction conditions are given, in outline, in Table 2. Details of experimental procedure, following irradiation, and analyses are given below.

Chloromonocarbonylbistriethylphosphine- π -cyclopentadienylmolybdenum(II).—After evaporation of the solvent under reduced pressure, the residue was redissolved in a

⁵ R. S. Nyholm, S. S. Sandhu, and M. H. B. Stiddard, *J. Chem. Soc.*, 1963, 5916.

⁶ R. Bramley, personal communication.

minimum of benzene-cyclohexane (1:1) and chromatographed on an alumina column. Elution with the same solvent mixture produced an orange solution. Evaporation of the solvent yielded the *product*, which was crystallised from benzene-isopentane, and dried *in vacuo* (Found: C, 47.0; H, 8.0; Cl, 7.9; P, 13.1. $C_{18}H_{35}ClMoOP_2$ requires C, 46.9; H, 7.7; Cl, 7.7; P, 13.4%).

Chlorodicarbonyltriphenylphosphine- π -cyclopentadienylmolybdenum(II).—Some crystals separated, but the bulk of the product was isolated on evaporation of the solvent. This was dissolved in a minimum of benzene and eluted from an alumina column with the same solvent. Evaporation of the eluate and crystallisation from benzene-isopentane yielded the *product*, which was dried *in vacuo* (Found: C, 58.6; H, 3.9; Cl, 6.8; P, 5.8. $C_{25}H_{20}ClMoO_2P$ requires C, 58.3; H, 3.9; Cl, 6.9; P, 6.0%).

Chloromonocarbonylbistriphenylphosphine- π -cyclopentadienylmolybdenum(II).—The *product*, which separated, was washed with isopentane, crystallised from benzene-isopentane, and dried *in vacuo* (Found: C, 67.0; H, 4.8; Cl, 5.0; P, 8.6. $C_{42}H_{35}ClMoOP_2$ requires C, 67.3; H, 4.7; Cl, 4.7; P, 8.3%).

Chlorodicarbonyltriphenylarsine- π -cyclopentadienylmolybdenum(II).—The orange crystals, which separated, and the residue after evaporation were dissolved in a minimum of benzene and eluted from an alumina column with the same solvent. Evaporation of the eluate and crystallisation of the residual solid from benzene-isopentane yielded the *compound*, which was dried *in vacuo* (Found: C, 54.0; H, 3.8; As, 13.5; Cl, 6.3. $C_{25}H_{20}AsClMoO_2$ requires C, 53.7; H, 3.6; As, 13.4; Cl, 6.3%).

Chloromonocarbonylbistriphenylarsine- π -cyclopentadienylmolybdenum(II).—Red crystals, which were deposited, were washed with isopentane. The *product* was obtained by crystallisation from benzene-isopentane, and dried *in vacuo* (Found: C, 60.1; H, 4.6; As, 17.7; Cl, 4.3. $C_{42}H_{35}As_2ClMoO$ requires C, 60.3; H, 4.2; As, 17.9; Cl, 4.2%).

Chlorodicarbonyltriphenylstibine- π -cyclopentadienylmolybdenum(II).—Orange crystals, which separated, and the residue after evaporation were dissolved in a minimum of benzene. Elution from an alumina column with the same solvent produced the *compound*, which was crystallised from benzene-isopentane, and dried *in vacuo* (Found: C, 49.8; H, 3.3; Cl, 5.9. $C_{25}H_{20}ClMoO_2Sb$ requires C, 49.6; H, 3.3; Cl, 5.9%).

Chloromonocarbonylbistriphenylstibine- π -cyclopentadienylmolybdenum(II).—The *product*, which separated, was washed with isopentane, crystallised from benzene-isopentane, and dried *in vacuo* (Found: C, 54.0; H, 3.5; Cl, 3.6. $C_{42}H_{35}ClMoOSb_2$ requires C, 54.2; H, 3.8; Cl, 3.8%).

1,2-Bisdiphenylphosphinoethanebis[chlorodicarbonyl- π -cyclopentadienylmolybdenum(II)].—The orange crystals, which were deposited, were filtered off, dissolved in a minimum of benzene-cyclohexane (2:1), and transferred to an alumina column. Elution with benzene produced three orange bands. The second, and most intense, band was collected, and after evaporation of the solvent, an orange residue remained. Crystallisation from benzene-isopentane produced the *compound*, which was dried *in vacuo* (Found: C, 53.4; H, 4.2; Cl, 7.8; P, 6.6. $C_{40}H_{34}Cl_2Mo_2O_4P_2$ requires C, 53.2; H, 3.8; Cl, 7.9; P, 6.9%).

Chloromonocarbonyl-1,2-bisdiphenylphosphinoethane- π -cyclopentadienylmolybdenum(II).—The filtrate from the previous preparation was evaporated and the residue crystallised from benzene-isopentane to yield the *product*,

which was dried *in vacuo* (Found: C, 61.5; H, 4.5; Cl, 4.8; P, 10.1. $C_{32}H_{25}ClMoOP_2$ requires C, 61.7; H, 4.7; Cl, 4.7; P, 10.0%).

Iododicarbonyltriethylphosphine- π -cyclopentadienylmolybdenum(II).—After evaporation of the solvent, the residual red solid was dissolved in cyclohexane (15 ml.) containing just sufficient of benzene to effect dissolution, and transferred to an alumina column. After elution with benzene-cyclohexane (1:2) and subsequent evaporation, a red solid was obtained. Crystallisation from benzene-isopentane yielded the *compound*, which was dried *in vacuo* (Found: C, 33.9; H, 4.5; I, 27.4; P, 6.9. $C_{13}H_{20}IMoO_2P$ requires C, 33.8; H, 4.4; I, 27.5; P, 6.7%).

Iodomocarbonylbistriethylphosphine- π -cyclopentadienylmolybdenum(II).—A red solid was obtained after evaporation of the solvent, dissolution in the minimum of benzene-cyclohexane (1:1), and chromatography on alumina using the same solvent mixture. The *product* was crystallised from benzene-isopentane, and dried *in vacuo* (Found: C, 39.3; H, 6.5; I, 23.0; P, 11.1. $C_{18}H_{35}IMoOP_2$ requires C, 39.2; H, 6.5; I, 23.0; P, 11.2%).

Iododicarbonyltricyclohexylphosphine- π -cyclopentadienylmolybdenum(II).—After evaporation of the solvent, the *product* was obtained by crystallisation from benzene-isopentane and dried *in vacuo* (Found: C, 48.1; H, 5.8; I, 20.3; P, 5.1. $C_{25}H_{38}IMoO_2P$ requires C, 48.1; H, 6.1; I, 20.3; P, 5.0%).

Iododicarbonyltriphenylphosphine- π -cyclopentadienylmolybdenum(II).—The crystals, which separated, and the residue after evaporation of the solvent were dissolved in benzene, and eluted from an alumina column with the same solvent. Evaporation and crystallisation from benzene-isopentane yielded the *product* which was dried *in vacuo* (Found: C, 49.8; H, 3.7; I, 20.8; P, 5.2. $C_{25}H_{20}IMoO_2P$ requires C, 49.5; H, 3.7; I, 20.8; P, 5.1%).

Iododicarbonyl(triphenyl phosphite)- π -cyclopentadienylmolybdenum(II).—The residue, after evaporation of the solvent, was dissolved in a minimum of benzene and transferred to an alumina column. Elution with benzene-cyclohexane (1:1) effected the separation of the compound. Evaporation and crystallisation from benzene-isopentane yielded the *product*, which was dried *in vacuo* (Found: C, 45.7; H, 3.5; I, 19.5; P, 4.7. $C_{25}H_{20}IMoO_3P$ requires C, 45.9; H, 3.1; I, 19.4; P, 4.7%).

Iodomocarbonylbis(triphenyl phosphite)- π -cyclopentadienylmolybdenum(II).—Evaporation of the solvent yielded a deep orange oil, which was dissolved in a minimum volume of cyclohexane-isopentane (1:1) containing a little benzene, and transferred to an alumina column. The chromatogram was eluted in turn with cyclohexane-isopentane (1:1), benzene-isopentane (1:1) to remove excess of ligand, and finally with benzene. Elution with benzene separated yellow and orange bands. The latter was collected and the solvent evaporated to yield an orange residue. Crystallisation from cyclohexane-isopentane yielded the *compound*, which was dried *in vacuo* (Found: C, 53.5; H, 3.7; I, 14.0; P, 6.1. $C_{42}H_{35}IMoO_7P_2$ requires C, 53.8; H, 3.7; I, 13.6; P, 6.6%).

Iododicarbonylmethyldiphenylarsine- π -cyclopentadienylmolybdenum(II).—Some red crystals separated and the remainder was obtained by evaporation of the solvent. Dissolution in a minimum of benzene, elution from an alumina column with the same solvent, and evaporation yielded the *product*, which was crystallised from benzene-isopentane, dried *in vacuo* (Found: C, 41.0; H, 3.2; As,

13.2; I, 21.5. $C_{20}H_{18}AsIMoO_2$ requires C, 40.8; H, 3.1; As, 12.8; I, 21.6%).

Iodomonomocarbonylbismethyldiphenylarsine- π -cyclopentadienylmolybdenum(II).—The brown residue, which remained after evaporation of the solvent, was dissolved in a minimum of benzene. After filtration of the solution, addition of isopentane precipitated red crystals, which were washed with the latter solvent, and dried *in vacuo* (Found: C, 47.6; H, 3.9; As, 18.5. $C_{32}H_{31}As_2IMoO$ requires C, 47.8; H, 3.9; As, 18.6%).

Iododicarbonyltriphenylarsine- π -cyclopentadienylmolybdenum(II).—After evaporation, the residual solid was dissolved in a minimum of benzene. Elution from an alumina column with the same solvent, evaporation, and crystallisation from benzene-isopentane yielded the *product*, which was dried *in vacuo* (Found: C, 46.4; H, 3.4; As, 11.8; I, 19.4. $C_{25}H_{20}AsIMoO_2$ requires C, 46.2; H, 3.1; As, 11.5; I, 19.5%).

Iododicarbonyltriphenylstibine- π -cyclopentadienylmolybdenum(II).—This complex was prepared as described for $C_5H_5Mo(CO)_2(SbPh_3)Cl$ (Found: C, 43.4; H, 3.2; I, 18.2. $C_{25}H_{20}IMoO_2Sb$ requires C, 43.1; H, 2.9; I, 18.2%).

Iodomonomocarbonylbistriphenylstibine- π -cyclopentadienylmolybdenum(II).—Red crystals, which separated, were dissolved in a minimum of benzene-cyclohexane (2:1) and eluted from alumina with the same mixture. After evaporation, the *product* was crystallised from benzene-isopentane, and dried *in vacuo* (Found: C, 49.5; H, 3.4; I, 11.9. $C_{42}H_{35}IMoOSb_2$ requires C, 49.3; H, 3.4; I, 12.2%).

Iodomonomocarbonyl-1,2-bisdiphenylphosphinoethane- π -cyclopentadienylmolybdenum(II).—The solution was concentrated and transferred to an alumina column. Elution with benzene-dichloromethane (2:1) produced a red band, which was collected. The eluate was evaporated to leave a red residue, which was crystallised from benzene-isopentane. Recrystallisation from dichloromethane-isopentane yielded the *compound*, which was dried *in vacuo* (Found: C, 53.6; H, 4.1; I, 17.9; P, 8.6. $C_{32}H_{29}IMoOP_2$ requires C, 53.8; H, 4.1; I, 17.8; P, 8.7%).

Iodomonomocarbonyl-o-phenylenebisdimethylarsine- π -cyclopentadienylmolybdenum(II).—After filtration, the solution was concentrated and transferred to an alumina column. After elution with benzene and subsequent evaporation of the solvent, a red solid remained. Crystallisation from benzene-isopentane yielded the *compound*, which was dried *in vacuo* (Found: C, 31.9; H, 3.6; As, 24.7; I, 20.6. $C_{16}H_{21}As_2IMoO$ requires C, 31.9; H, 3.5; As, 24.9; I, 21.1%).

Dicarbonylbistriethylphosphine- π -cyclopentadienylmolybdenum(II) Perchlorate.—A solution of $C_5H_5Mo(CO)_3Cl$ (0.40 g.) and PEt_3 (0.90 g.) in benzene (25 ml.) was allowed to stand for 2 weeks in an evacuated tube at room temperature. The crystals, which separated, were filtered off, washed with cold methanol, dried *in vacuo*, and dissolved

in a minimum of acetone. Addition of a saturated solution of $LiClO_4$ in acetone precipitated the product (0.30 g.) which was crystallised from acetone-ether and dried *in vacuo* (Found: C, 40.9; H, 6.4; Cl, 6.6; P, 10.9. $C_{19}H_{35}ClMoO_6P_2$ requires C, 41.3; H, 6.4; Cl, 6.4; P, 11.2%).

Dicarbonylbistriphenylphosphine- π -cyclopentadienylmolybdenum(II) Perchlorate.—A solution of $C_5H_5Mo(CO)_3Cl$ (0.56 g.), PPh_3 (1.06 g.), and anhydrous $AlCl_3$ (0.86 g.) in benzene (50 ml.) was exposed to ultraviolet light for 40 hr. A yellow material, which separated, was dissolved in a minimum of acetone. A slight excess of $LiClO_4$ in acetone was added. The *product* (0.53 g.) was precipitated by addition of water, recrystallised from acetone-ether, and dried *in vacuo* (Found: C, 61.1; H, 4.4; Cl, 4.1; P, 7.4. $C_{43}H_{35}ClMoO_6P_2$ requires C, 61.4; H, 4.2; Cl, 4.2; P, 7.4%).

Dicarbonyl-1,2-bisdiphenylphosphinoethane- π -cyclopentadienylmolybdenum(II) Perchlorate.—A solution of $C_5H_5Mo(CO)_3Cl$ (0.40 g.) and the diphosphine (0.60 g.) in benzene (30 ml.) was allowed to stand for 2 weeks at room temperature. The yellow crystals, which separated, were washed with cold methanol, and dried *in vacuo*. The *perchlorate* (0.25 g.) was obtained by addition of $LiClO_4$ in acetone, precipitation by addition of water, and drying *in vacuo* (Found: C, 55.2; H, 3.9; Cl, 5.2; P, 8.8. $C_{33}H_{29}ClMoO_6P_2$ requires C, 55.4; H, 4.1; Cl, 5.0; P, 8.7%).

Dicarbonyl-o-phenylenebisdimethylarsine- π -cyclopentadienylmolybdenum(II) Iodide.—The yellow crystals, which separated, and the residue after evaporation, were crystallised from acetone-ether to yield the *product*, which was dried *in vacuo* (Found: C, 32.5; H, 3.8; As, 23.5; I, 19.7. $C_{17}H_{21}As_2IMoO_2$ requires C, 32.4; H, 3.4; As, 23.8; I, 20.1%).

Properties of Compounds.—All the compounds except $C_5H_5Mo(CO)(AsPh_2Me)_2I$ were stable in air, but solutions tend to decompose. They are soluble in acetone and chloroform, but insoluble in light petroleum. The salts are also insoluble in benzene, while other compounds dissolve in this solvent. With the exception of (I), (X), (XI), (XIV), and (XV), all compounds are insoluble in cyclohexane.

Physical Measurements.—Infrared spectra were measured on Grubb-Parsons G.S.2A and DM2 and Perkin-Elmer 337 spectrophotometers. Molecular weights were determined with a Mechrolab Vapour-pressure Osmometer, model 301A. Proton magnetic resonance spectra were measured on Perkin-Elmer 60 Mc./sec. and Varian 100 Mc./sec. instruments.

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