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Reactions of-π-Indenyl Complexes of Transition Metals. III.[1] Kinetics and Mechanisms of Substitution Reactions of Tricarbonyl-π-indenylhalomolybdenum(II) Complexes

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Received April 30, 1970

Observed rate constants for reactions of the complexes π–$C_9H_7Mo(CO)_3X$ *(*$X = Cl, Br, I$*) with phosphorus ligands (L):*

$$\pi\text{–}C_9H_7Mo(CO)_3X + L \longrightarrow \pi\text{–}C_9H_7Mo(CO)_2LX + CO$$

can be fitted to the expression:

$$k_{obs} = k_A + k_B[L]$$

where, for a given complex, solvent and temperature, k_A *is independent of the nature and concentration of the ligand, but the values of* k_B *increase in the order:*

$$L = P(OPh)_3 < L = PPh_3 < L = P(OMe)_3 < L = PBu^n_3$$

The k_A *term represents a dissociative reaction mechanism, while the* k_B *term represents an associative mechanism. By comparison, those of the corresponding reactions of the π–cyclopentadienyl complexes* π–$C_5H_5Mo(CO)_3X$ *for which reproducible kinetic data could be obtained obeyed the simpler rate expression*

$$k_{obs} = k_A$$

The values of k_A *for the π–indenyl complexes are several thousand times greater than those for the corresponding π–cyclopentadienyl complexes, due to the lower values of* ΔH^**. The observation of an associative pathway for the reactions of the π–indenyl complexes, but not for the π–cyclopentadienyl complexes, is the reverse of what would be expected on steric grounds. Possible explanations for both these effects are suggested. In both cases it is proposed that the six-membered aromatic ring of the π-indenyl ligand plays a crucial role.*

Introduction

It is well known that the rate and mechanism of a ligand substitution reaction in a transition metal complex can be greatly affected by alteration of a ligand on the metal which is neither the entering nor the leaving group in the reaction. Studies of such effects have in the past mainly been confined to ligands which can be thought of as two-electron donors occupying one coordination site on the metal.

This paper lists rate constants and activation parameters for carbon monoxide replacement reactions of the type:

$$\pi\text{–}C_9H_7Mo(CO)_3X + L \longrightarrow \pi\text{–}C_9H_7Mo(CO)_2LX + CO \qquad (1)$$

(where X = Cl, Br or I, and L is a phosphorus(III) ligand). The reasons for the striking differences, both in mechanism and in rate, between these reactions and those of the analogous π–cyclopentadienyl complexes:[2]

$$\pi\text{–}C_5H_5Mo(CO)_3X + L \longrightarrow \pi\text{–}C_5H_5Mo(CO)_2LX + CO \qquad (2)$$

are discussed.

Experimental Section

Preparation and purification of ligands and solvents have been discussed in an earlier paper,[2] as have the techniques used to treat kinetic data.[3] Starting materials and products of the reactions studied were characterized in the previous paper in this series,[1] except for π–$(CH_3O)_2C_9H_5Mo(CO)_3I$, which was prepared from $[\pi\text{–}(CH_3O)_2C_9H_5Mo(CO)_3]_2$[3] by reaction with iodine, using the technique previously described[1] for the preparation of π–$C_9H_7Mo(CO)_3I$. Four methods were used to obtain rate constants: (i) measuring the rate of disappearance of the highest frequency carbonyl stretching band in the infra-red spectra of the complexes π–$C_9H_7Mo(CO)_3X$, (ii) measuring the rate of appearance of a similar band in the spectrum of a reaction product, (iii) measuring the rate of change of absorbance at a particular wavelength in the visible/near ultra-violet spectrum of a reaction mixture, and (iv) measuring the rate of carbon monoxide evolution. A Perkin-Elmer 257 spectrophotometer was used for infra-red work, a Cary 14 spectrophotometer for visible/near ultra-violet work, and an aparatus similar to that described by Calderazzo and Cotton[4] for carbon monoxide evolution studies.

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(1) Part II, A. J. Hart-Davis, C. White, and R. J. Mawby, *Inorg. Chim. Acta*, *4*, 431 (1970).

(2) C. White and R. J. Mawby, *Inorg. Chim. Acta*, *4*, 261 (1970).

(3) A. J. Hart-Davis and R. J. Mawby, *J. Chem. Soc.* (*A*), 1969, 2403.

(4) F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, *1*, 30 (1962).

Table I. Observed Rate Constants for Reactions of π–$C_9H_7Mo(CO)_3I$ with Various Ligands

Solvent	Temp. (°C)	Ligand	Ligand Concentration (M)	10^4 k_{obs} (sec^{-1})
Tetrahydrofuran	20.1	$P(OPh)_3$	0.153	0.428
			0.258	0.437
			0.382	0.461
			0.708	0.491
		$P(OMe)_3$	0.189	3.14
			0.304	4.66
			0.585	8.79
	30.0	PPh_3	0.099	1.75
			0.196	1.83
			0.519	2.02
			0.814	2.39
		PBu^n_3	0.106	7.20
			0.190	9.47
			0.361	16.5
			0.373	18.2
			0.666	29.8
		$P(OPh)_3$	0.177	1.81
			0.335	1.85
			0.514	1.89
		$P(OMe)_3$	0.304	10.1
			0.333	11.0
			0.551	17.2
	40.0	$P(OPh)_3$	0.112	6.62
			0.240	6.69
			0.498	6.79
		$P(OMe)_3$	0.231	20.1
			0.415	32.7
			0.657	49.6
Benzene	30.0	$P(OPh)_3$	0.163	1.41
			0.244	1.51
			0.521	1.75
			0.824	1.99
		$P(OMe)_3$	0.102	5.98
			0.167	8.85
			0.194	10.5
			0.289	15.6
			0.567	31.3
			0.643	36.4
			0.775	41.4
			0.949	52.3
Chloroform	30.0	$P(OPh)_3$	0.143	1.42
			0.235	1.53
			0.483	1.73
			0.729	1.92
Chloroform	30.0	$P(OMe)_3$	0.129	4.60
			0.137	5.53
			0.271	9.20
			0.329	10.7
			0.401	14.7
			0.544	21.3
			0.776	29.6
Acetonitrile	30.0	$P(OPh)_3$	0.192	3.46
			0.347	3.39
			0.614	3.32
		$P(OMe)_3$	0.087	5.64
			0.121	7.31
			0.425	15.9

Concentrations of molybdenum complexes were around 0.01 M, except for reactions followed by visible/ultra-violet spectroscopy, where concentrations of 0.002 M were used. Ligand concentrations were always at least ten times greater than those of molybdenum complexes. All reactions were found to be first order in molybdenum complex, and reliable kinetic data could be obtained from at least the first 2½ half lives. Rate constants were found to be reproducible to within ±4%.

Results

Two immediate differences are observable between the behaviour of complexes π–$C_5H_5Mo(CO)_3X$ and π–$C_9H_7Mo(CO)_3X$ with phosphorus(III) ligands. Unlike the reactions of the π–cyclopentadienyl compounds, those of π–indenyl compounds are not affected — in rate or in product distribution — by light. Secondly, in none of the reactions of π-indenyl complexes studied were there the complications

Table II. Observed Rate Constants for Reactions of π–$C_9H_7Mo(CO)_3Br$ with Various Ligands

Solvent	Temp. (°C)	Ligand	Ligand Concentration (*M*)	$10^4\ k_{obs}$ (sec^{-1})
Tetrahydrofuran	5.0	$P(OMe)_3$	0.065	2.62
			0.149	4.22
			0.222	5.55
			0.286	6.64
			0.391	8.52
			0.422	8.98
	8.8	PPh_3	0.046	3.25
			0.093	3.25
			0.140	3.40
			0.287	3.96
			0.298	4.03
	10.0	$P(OMe)_3$	0.094	6.61
			0.208	9.26
			0.248	11.2
			0.410	15.6
	15.0	PPh_3	0.097	8.04
			0.146	8.45
			0.230	8.82
			0.299	9.08
			0.388	9.68
	15.0	PBu^n_3	0.094	16.3
			0.135	21.2
			0.195	28.0
			0.248	32.3
			0.317	40.3
		$P(OPh)_3$	0.105	7.87
			0.223	8.12
			0.296	8.22
		$P(OMe)_3$	0.098	12.6
			0.133	14.0
			0.193	16.4
			0.231	17.7
			0.297	20.4
	19.5	$P(OMe)_3$	0.099	20.6
			0.153	23.7
			0.192	26.4
			0.231	28.3
			0.300	33.0
	20.0	PPh_3	0.075	15.2
			0.152	15.8
			0.256	16.6
			0.366	16.7
			0.389	18.3
	25.7	PPh_3	0.041	34.9
			0.082	35.1
			0.216	37.4
			0.294	38.1
Benzene	15.0	PPh_3	0.093	6.84
			0.177	7.31
			0.249	7.55
			0.346	8.02
		$P(OMe)_3$	0.106	15.2
			0.163	20.0
			0.207	23.7
			0.243	26.9
			0.332	32.6
Acetone	15.0	PPh_3	0.098	10.8
			0.217	11.1
			0.338	11.2
		$P(OMe)_3$	0.109	14.3
			0.184	17.6
			0.277	21.7
			0.378	26.2

of induction periods and variable reaction rates previously observed for some reactions of π–$C_5H_5Mo(CO)_3Br$ and π–$C_5H_5Mo(CO)_3I$.[2]

Observed rate constants for reactions of π–$C_9H_7Mo(CO)_3I$ are collected in Table I, while those for π–$C_9H_7Mo(CO)_3Br$ are in Table II. The reactions of π–$C_9H_7Mo(CO)_3Cl$ were too rapid at room temperature to study by conventional means, and the results of a limited study at 10°C are given in Table III. All observed rate constants for a given molybdenum complex, solvent, and temperature could be fitted to the expression

$$k_{obs} = k_A + k_B[L]$$

Table III. Observed Rate Constants[a] for Reactions of π—$C_9H_7Mo(CO)_3Cl$, and Values of k_A and k_B, where $k_{obs} = k_A+k_B[L]$

Ligand	Ligand Concentration (M)	10^4 k_{obs} (sec^{-1})	10^4 k_A (sec^{-1})	10^4 k_B (M^{-1} sec^{-1})
PPh_3	0.099	66.3	65.3(±0.2)	10.7(± 0.4)
	0.289	68.4		
	0.392	69.4		
$P(OMe)_3$	0.100	77.7	69 (±3)	89 (±13)
	0.163	84.3		
	0.203	85.4		
	0.233	92.4		
	0.292	94.2		

[a] All reactions performed in tetrahydrofuran at 10°C.

Table IV. Values of k_A and k_B, where $k_{obs} = k_A+k_B[L]$, for Reactions of π—$C_9H_7Mo(CO)_3I$ with Various Ligands

Solvent	Temperature (°C)	Ligand	10^4 k_A (sec^{-1})	10^4 k_B (M^{-1} sec^{-1})
Tetrahydrofuran	20.1	$P(OPh)_3$	0.41(±0.01)	0.11(±0.01)
		$P(OMe)_3$	0.45(±0.08)	14.1 (±0.4)
	30.0	PPh_3	1.6 (±0.1)	0.88(±0.10)
		PBu^n_3	1.8 (±1.0)	42 (±2)
		$P(OPh)_3$	1.77(±0.03)	0.24(±0.02)
		$P(OMe)_3$	1.6 (±0.3)	29.3 (±1.0)
	40.0	$P(OPh)_3$	6.58(±0.03)	0.47(±0.07)
		$P(OMe)_3$	[a]	67 (±3)
Benzene	30.0	$P(OPh)_3$	1.3 (±0.3)	0.85(±0.20)
		$P(OMe)_3$	[a]	56 (±5)
Chloroform	30.0	$P(OPh)_3$	1.3 (±0.2)	0.79(±0.08)
		$P(OMe)_3$	[a]	33 (±7)
Acetonitrile	30.0	$P(OPh)_3$	3.50(±0.03)	0
		$P(OMe)_3$	3.5 (±0.5)	29 (±3)

[a] Slope of plot of k_{obs} versus [L] was too steep to allow a meaningful value for k_A to be obtained.

Table V. Values of k_A and k_B, where $k_{obs} = k_A+k_B[L]$, for the Reactions of π—$C_9H_7Mo(CO)_3Br$ with Various Ligands

Solvent	Temperature (°C)	Ligand	10^4 k_A (sec^{-1})	10^4 k_B (M^{-1} sec^{-1})
Tetrahydrofuran	5.0	$P(OMe)_3$	1.53(±0.06)	17.8(±0.2)
	8.8	PPh_3	3.02(±0.07)	3.2(±0.3)
	10.0	$P(OMe)_3$	4.0 (±0.2)	28.6(±0.6)
	15.0	PPh_3	7.6 (±0.1)	5.3(±0.4)
		PBu^n_3	7 (±1)	106 (±3)
		$P(OPh)_3$	7.68(±0.05)	1.9(±0.2)
		$P(OMe)_3$	8 (±1)	39 (±1)
	19.5	$P(OMe)_3$	14.4 (±0.3)	61 (±2)
	20.0	PPh_3	14.6 (±0.6)	8 (±1)
	25.7	PPh_3	34.2 (±0.3)	13.5(±1.3)
Benzene	15.0	PPh_3	6.45(±0.06)	4.6(±0.3)
		$P(OMe)_3$	7.3 (±0.8)	78 (±3)
Acetone	15.0	PPh_3	10.6 (±0.2)	2.0(±0.6)
		$P(OMe)_3$	9.4 (±1.0)	44.4(±1.3)

Table VI. Activation Data for the First- and Second-Order Parts of Reactions of π—$C_9H_7Mo(CO)_3X$ (X=Br and I) in Tetrahydrofuran, with Comparative Data for π—$C_5H_5Mo(CO)_3X$ in Diglyme.

Complex	Ligand	First-Order (k_A)		Second-Order (k_B)	
		ΔH*	ΔS*	ΔH*	ΔS*
π—$C_9H_7Mo(CO)_3I$	$P(OPh)_3$	25.5(±0.4)	+8.4(±0.6)	13.3(±0.7)	−35.7(±0.8)
	$P(OMe)_3$			13.7(±0.8)	−25 (±1)
π—$C_5H_5Mo(CO)_3I$	PPh_3	29.6(±0.6)	+6.0(±0.6)	[a]	
π—$C_9H_7Mo(CO)_3Br$	PPh_3	23.2(±0.5)	+7.6(±0.5)	13.5(±0.6)	−26.7(±0.5)
	$P(OMe)_3$			12.8(±0.8)	−24.8(±0.7)
π—$C_5H_5Mo(CO)_3Br$	PPh_3	28.9(±0.2)	+10.0(±0.4)	[a]	

[a] These reactions operate entirely by a first-order process.

where k$_A$ was constant (within experimental error) for all ligands, but k$_B$ increased in the order

$$L = P(OPh)_3 < L = PPh_3 < L = P(OMe)_3 < L = PBu^n{}_3$$

Computed « best-fit » values of k$_A$ and k$_B$, together with the uncertainties in the values, are collected for the reactions of π–C$_9$H$_7$Mo(CO)$_3$I in Table IV, and for π–C$_9$H$_7$Mo(CO)$_3$Br in Table V. Values for π–C$_9$H$_7$Mo(CO)$_3$Cl have been included in Table III.

Because of the small variation of k$_{obs}$ with ligand concentration, the rate constants for P(OPh)$_3$ or PPh$_3$ give the most accurate values for k$_A$, and these have been used in calculating the first order activation parameters which are listed in Table VI, together with the activation parameters for the second order (k$_B$) part of reactions. Comparative data for the analogous π-cyclopentadienyl complexes are also given.

Discussion

The rate expression

$$k_{obs} = k_A + k_B[L] \qquad (3)$$

suggests that the carbonyl replacement reactions (1) take place by two competing mechanisms, one of which is first order overall, the other second order. By comparison, the rates for the analogous reactions of the π–cyclopentadienyl complexes π–C$_5$H$_5$Mo(CO)$_3$X (X = Cl, Br, I) fit the simpler expression

$$k_{obs} = k_A \qquad (4)$$

being (except for the special case of reactions with PBu$^n{}_2$Ph and PBu$^n{}_3$) independent of the nature and concentration of the ligand used.[2]

The two mechanisms for the reactions of the π-indenyl complexes will be discussed separately.

The first order process. Tables IV and V show that the value of k$_A$ varies little from solvent to solvent, suggesting that the mechanism involved is truly dissociative, rather than an associative mechanism with the solvent acting as the nucleophile. Table VI shows that the entropy of activation for this process is positive, the ΔS^* values being similar to those for the analogous reactions of π–C$_5$H$_5$Mo(CO)$_3$)X. This also suggests a dissociative mechanism similar to that which is the sole mechanism for the reactions of the π-cyclopentadienyl complexes.[2]

$$\pi\text{–}C_9H_7Mo(CO)_3Cl \xrightarrow[-CO]{slow} \pi\text{–}C_9H_7Mo(CO)_2Cl \xrightarrow[+L]{fast} \pi\text{–}C_9H_7Mo(CO)_2LCl \qquad (5)$$

The values of k$_A$ at a given temperature are appreciably larger for reactions of π–C$_9$H$_7$Mo(CO)$_3$Br than those of π–C$_9$H$_7$Mo(CO)$_3$I. This increase in rate is due to a drop in ΔH^* from 25.5 to 23.2 kcal/mole. Since most of the activation enthalpy in a dissociative process is taken up in bond breaking, this implies that the Mo–CO bond is stronger in π–C$_9$H$_7$Mo(CO$_3$I than in π–C$_9$H$_7$Mo(CO)$_3$Br. This is in agreement with the rise in frequency of the highest energy carbonyl stretching band (π–C$_9$H$_7$Mo(CO)$_3$I, 2043; π–C$_9$H$_7$Mo(CO)$_3$Br, 2052; π–C$_9$H$_7$Mo(CO)$_3$Cl, 2063 cm^{-1}). A similar effect is noticeable for the complexes π–C$_5$H$_5$Mo(CO)$_3$X (X = Cl, Br, I).[2]

The similarity in mechanism for the two series of complexes is not matched by a similarity in rate. The reactions of the π-indenyl complexes are so much faster than those of the π-cyclopentadienyl complexes that one can only compare rates by extrapolating from rate constants obtained at much higher temperatures for the latter reactions. Using these extrapolated rate constants, one obtains the following *relative* values of k$_A$ at 10°C.

π–C$_5$H$_5$Mo(CO)$_3$I	π–C$_5$H$_5$Mo(CO)$_3$Br	π–C$_5$H$_5$Mo(CO)$_3$Cl
1	23	614
π–C$_9$H$_7$Mo(CO)$_3$I	π–C$_9$H$_7$Mo(CO)$_3$Br	π–C$_9$H$_7$Mo(CO)$_3$Cl
6,600	211,000	3,580,000

Reference to Table VI shows that the vast differences in rate between the two series can be attributed predominantly to the much lower activation enthalpies of the π-indenyl complexes. There is nothing to suggest a difference in ground state Mo–CO bond strengths between the complexes π–C$_9$H$_7$Mo(CO)$_3$X and π–C$_5$H$_5$Mo(CO)$_3$X large enough to cause this effect: in fact, the infra-red spectra of the two series of compounds in the C–O stretching region are virtually identical,[1] the differences between chloro-, bromo- and iodo-complex in a given series being much larger than the difference between a pair of complexes, one π-indenyl and one π-cyclopentadienyl, with the same halogen.

This suggests that the difference in rate, and in activation enthalpy, must be due to a marked difference in stability of the activated states for the two series of complexes. The presence of the π-indenyl ligand appears to stabilize the activated state for the dissociative process in a way that is not possible for the π-cyclopentadienyl ligand. The crystal structure[5] of π–C$_9$H$_7$Mo(CO)$_3$I shows the π-indenyl ligand to be planar, with the six-membered ring too far from the molybdenum to be involved in bonding or to cause noticeable steric effects. Stabilization of the transition state could be caused either by a change in the geometry of the bonding between indenyl ligand and metal, or by a redistribution of electron density between the indenyl ligand and the rest of the complex (which might be expected to occur more easily with the polarizable indenyl ligand than with the cyclopentadienyl ligand).

In order to test the second of these possibilities, the 5,6-dimethoxyindenyl complex, π-(CH$_3$O)$_2$C$_9$H$_5$Mo(CO)$_3$I, was synthesized. The presence of the electron-releasing methoxy-groups should have a considerable effect on the rate of any reaction which involves a redistribution of electron density between ground and transition state. In fact, the difference in rate between the reactions of π-C$_9$H$_7$Mo(CO)$_3$I and

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(5) A. Mawby and G. E. Pringle, personal communication.

π–$(CH_3O)_2C_9H_5Mo(CO)_3I$ at 30°C is only a factor of three, compared with the factor of 6,600 between the rates of π–$C_5H_5Mo(CO)_3I$ and π–$C_9H_7Mo(CO)_3I$. If appreciable movement of charge occurred during the approach to the transition state, one would expect the methoxy-groups to have a far greater effect. A further piece of evidence against a substantial charge migration is the absence of any marked solvent dependence in the value of k_A (see Tables IV and V).

This leaves the alternative explanation, a change in the mode of bonding between π-indenyl ligand and metal. Stabilization of the transition state could be achieved by a measure of bonding between *six-membered* ring and metal, to compensate for the loss of the carbonyl group. This could arise from loss of planarity in the indenyl ligand, with the six-membered ring bending in towards the metal, or from a slight movement of the molybdenum atom towards a more central position above a planar indenyl ligand.

The second order process. The most striking point about this process, which presumably represents nucleophilic attack on molybdenum simultaneous with loss of a carbonyl group, is that no such process is observed for any of the analogous reactions of the π-cyclopentadienyl complexes π–$C_5H_5Mo(CO)_3X$.[2] Only the reactions of π–$C_5H_5Mo(CO)_3Cl$ with L = $PBu^n{}_2Ph$ and $PBu^n{}_3$ to yield $Mo(CO)_3L_3$ and $C_5H_5L^+$ (which probably involved nucleophilic attack on the cyclopentadienyl ligand rather than the metal, and were strongly solvent-dependent in rate) gave second-order kinetics. (The reactions of π-$C_9H_7Mo(CO)_3X$ (X = Br, I) with $PBu^n{}_3$ also yielded small quantities of $Mo(CO)_3(PBu^n{}_3)_3$ and $Mo(CO)_4(PBu^n{}_3)_2$, so that a small part of the k_B terms for the reactions with $PBu^n{}_3$ may represent nucleophilic attack on the π-indenyl ligand rather than on molybdenum. For this reason the exact values of k_B for these two reactions are not strictly comparable with the k_B values for other ligands.

The relatively low activation enthalpies and large negative entropies of activation listed in Table VI for the second order process are typical of an associative mechanism. It is interesting to note that there is little dependence of k_B values on solvent (see values for the reactions with $P(OMe)_3$ listed in Tables IV and V).

Clearly the replacement of the π-cyclopentadienyl ligand by the π-indenyl ligand has made nucleophilic attack on molybdenum much easier. This is the reverse of what one would expect on steric grounds. The phenomenon of easier nucleophilic attack in π-indenyl complexes has already been observed for the reactions of π-$C_9H_7Mo(CO)_3Me$.[3] The small effect of solvent on the size of k_B makes any process involving migration of negative charge on to the indenyl ligand during nucleophilic attack unlikely. A more likely explanation would seem to be that advanced (see Figure, reference 3) for the reactions of π-$C_9H_7Mo(CO)_3Me$. A small sideways displacement of the indenyl ligand with respect to the molybdenum atom transforms the bonding to an allyl system, freeing an orbital on the molybdenum atom for interaction with the incoming nucleophile. The six-membered ring of the indenyl ligand retains its full resonance energy during the transformation. The failure to observe an associative mechanism for the π-cyclopentadienyl complexes is presumably due to the fact that a similar transformation would leave an isolated double bond in the five-membered ring.

Conclusion

The explanations for the increased rate of the first-order process and the observation of a second-order process for the reactions of π-$C_9H_7Mo(CO)_3X$ (X = Cl, Br, I) depend crucially on the presence of the aromatic six-membered ring in the indenyl ligand.. Experiments designed to demonstrate the importance of the aromatic character of this ring are at present in progress.

Acknowledgements. We thank the SRC for maintenance grants to A. J. H. D. and C. W. We are grateful to Mrs C. A. Thomas for experimental assistance, and to Drs A. Mawby and G. E. Pringle for information, prior to publication, on the structure of π-$C_9H_7Mo(CO)_3I$.