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Reactions of π-Indenyl Complexes of Transition Metals. II.[1] Preparation and Reactions of Tricarbonyl-π-indenylhalomolybdenum(II) Complexes

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The preparation is reported of the complexes π–$C_9H_7Mo(CO)_3Cl$, π–$C_9H_7Mo(CO)_3Br$ and π–$C_9H_7Mo(CO)_3I$, the physical properties of the last named compound being identical to those of the previously reported π–$C_9H_7Mo(CO)_2I$. All three complexes react with phosphorus(III) ligands L to form compounds π–$C_9H_7Mo(CO)_2LX$, which probably have the ligands L and X cis *to one another.*

All three complexes, and π-$C_5H_5Mo(CO)_3I$, can be converted to new compounds believed to be [π-$C_9H_7Mo(CO)_2X]_2$ (X= Cl, Br, and I) and [π-$C_5H_5Mo(CO)_2I]_2$.

Introduction

This paper describes the preparation of halotricarbonyl-π-indenylmolybdenum(II) complexes, π–$C_9H_7Mo(CO)_3X$ (X = Cl, Br and I), and a study of their physical properties and chemical reactions, as part of a general study[1] of the effects of the π–indenyl ligand on the reactions of transition metals.

Experimental Section

Ligands. Details of preparations and purifications are given in an earlier paper.[2]

Preparation of Complexes. (Petroleum ether used in preparations had a 40-60°C boiling range except where otherwise stated).

[π–$C_9H_7Mo(CO)_3]_2$. This was prepared by the method of King and Bisnette,[3] except that petroleum ether (120-160°C) was used as solvent instead of the expensive ethylcyclohexane.

π–$C_9H_7Mo(CO)_3Cl$. [π–$C_9H_7Mo(CO)_3]_2$ (1.0 g) in $CHCl_3$ (20 ml) was irradiated under an atmosphere of CO with two 60 w light bulbs for 5 hr at 30°C. After removal of the solvent under vacuum, the residue was purified by chromatography on silica gel, using CH_2Cl_2/petroleum ether mixtures as eluent, and recrystallized from CH_2Cl_2/hexane. Yield 45%. π–$C_9H_7Mo(CO)_3Br$ was prepared in the same way using $CHBr_3$, with a reaction time of 2 hr. Yield 55%.

π–$C_9H_7Mo(CO)_3I$. This was first prepared by the exact method described by King and Bisnette[3] for π–$C_9H_7Mo(CO)_2I$. In subsequent preparations the product was separated from excess iodine by chromatography on silica gel, using CH_2Cl_2/petroleum mixtures as eluent, before recrystallisation from CH_2Cl_2/hexane. Both procedures gave exactly the same product. The crystal used for the X-ray structure determination[4] (see Results section) came from the original preparation, and crystals from a subsequent preparation gave identical X-ray data.

π–$C_9H_7Mo(CO)_2LX$. These complexes (X = halogen; L = phosphorus ligand) were prepared by mixing π–$C_9H_7Mo(CO)_3X$ with a slight excess of the ligand in tetrahydrofuran (dichloromethane for the iodo-complexes). Typical reaction conditions were 1 hr at 10°C for X = Cl, 2 hr at room temperature for X = Br, and 24 hr at room temperature for X = I. Yields were virtually quantitative. Complexes were purified by chromatography on silica gel and recrystallised in most cases from CH_2Cl_2/hexane.

Reactions of π–$C_9H_7Mo(CO)_3X$ (X = Br, I) with PBu^n_3. These were performed in the same way as reactions with the other ligands, but chromatography on silica gel yielded small amounts of *fac*–$Mo(CO)_3(PBu^n_3)_3$ and *cis*–$Mo(CO)_4(PBu^n_3)_2$ on elution with hexane,[2] before elution of the « normal » product, π–$C_9H_7Mo(CO)_2(PBu^n_3)X$, with CH_2Cl_2/petroleum ether.

[π–$C_9H_7Mo(CO)_2X]_n$. These complexes (X = Cl, Br and I) were prepared by heating the complexes π–$C_9H_7Mo(CO)_3X$ under high vacuum at 100°C for 24 hr. Purification proved impossible, but the red powder obtained by heating π–$C_9H_7Mo(CO)_3Cl$ was formed with little apparent decomposition, and analytical data are given for the crude product.

[π–$C_5H_5Mo(CO)_2I]_n$. π–$C_5H_5Mo(CO)_3I$ (0.15 g) in hexane (80 ml) was irradiated for 3 hr with a 125 w ultra-violet lamp. The dark brown powder obtained was removed by filtration and washed with a little hexane.

Analytical data are given in Table I.

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(2) C. White and R. J. Mawby, *Inorg. Chim. Acta*, *4*, 331 (1970).
(3) R. B. King and M. B. Bisnette, *Inorg. Chem.*, *4*, 475 (1965).
(4) A. Mawby and G. E. Pringle, personal communication.

Table I. Analytical Data

	Colour	M.Pt. °C	Found %C	Found %H	Found %X[a]	Calculated %C	Calculated %H	Calculated %X[a]
π—$C_9H_7Mo(CO)_3Cl$	orange	98[d]	43.4	2.2	10.6	43.6	2.1	10.7
π—$C_9H_7Mo(CO)_3Br$	red	98[d]	38.4	2.0	21.5	38.4	1.9	21.3
π—$C_9H_7Mo(CO)_3I$	red-brown	143-4[d]	33.9	2.1	31.6	34.1	1.7	30.1
π—$C_9H_7Mo(CO)_2(PPh_3)Cl$	red	144[d]	61.4	4.0		61.7	3.9	
π—$C_9H_7Mo(CO)_2(P\{OMe\}_3)Cl$	red	87-8	36.6	3.8	8.3	39.4	3.8	8.3
π—$C_9H_7Mo(CO)_2(PPh_3)Br$	red	156[d]	57.2	3.9		57.2	3.6	
π—$C_9H_7Mo(CO)_2(PBu^n_3)Br$	red	98-9	49.7	6.1		50.3	6.2	
π—$C_9H_7Mo(CO)_2(P\{OPh\}_3)Br$	red	138	53.7	3.7	12.0	53.0	3.4	12.1
π—$C_9H_7Mo(CO)_2(PPh_3)I$	red	180[d]	53.4	3.5	19.1	53.1	3.4	19.3
π—$C_9H_7Mo(CO)_2(PBu^n_3)I$	red	80[d]	46.3	5.9		46.3	5.8	
π—$C_9H_7Mo(CO)_2(P\{OPh\}_3)I$	red	145[d]	49.0	3.2		49.5	3.2	
π—$C_9H_7Mo(CO)_2(P\{OMe\}_3)I$	red	113[d]	33.2	3.2		32.5	3.1	
$[\pi$—$C_9H_7Mo(CO)_2Cl]_n$[b]	red	—	42.6	2.4		43.7	2.3	

[a] X = halogen; [b] unpurified sample; [d] melts with decomposition.

Table II. Infra-red Spectra of π—Indenyl Complexes in the C—O Stretching Region (with Spectra for some Analogous π—Cyclopentadienyl Complexes)

	cm^{-1}
π—$C_9H_7Mo(CO)_3Cl$	2063, 1995, 1963[a]
π—$C_5H_5Mo(CO)_3Cl$	2062, 1992, 1967[b]
π—$C_9H_7Mo(CO)_3Br$	2052, 1988, 1957[b]
π—$C_5H_5Mo(CO)_3Br$	2052, 1986, 1965[b]
π—$C_9H_7Mo(CO)_3I$	2043, 1981, 1957[b]
π—$C_5H_5Mo(CO)_3I$	2045, 1979, 1965[b]
π—$C_9H_7Mo(CO)_2(PPh_3)Cl$	1972, 1886[a]
π—$C_9H_7Mo(CO)_2(P\{OMe\}_3)Cl$	1987, 1901[a]
π—$C_9H_7Mo(CO)_2(PPh_3)Br$	1974, 1889[a]
π—$C_9H_7Mo(CO)_2(PBu^n_3)Br$	1964, 1887[a]
π—$C_9H_7Mo(CO)_2(P\{OPh\}_3)Br$	1994, 1918[a]
π—$C_9H_7Mo(CO)_2(P\{OMe\}_3)Br$	1983, 1901[a]
π—$C_9H_7Mo(CO)_2(PPh_3)I$	1970, 1890[a]
π—$C_9H_7Mo(CO)_2(PBu^n_3)I$	1961, 1880[a]
π—$C_9H_7Mo(CO)_2(P\{OPh\}_3)I$	1988, 1917[a]
π—$C_9H_7Mo(CO)_2(P\{OMe\}_3)I$	1981, 1905[a]
$[\pi$—$C_9H_7Mo(CO)_2Cl]_n$	1970, 1873[c]
$[\pi$—$C_9H_7Mo(CO)_2Br]_n$	1962, 1868[c]
$[\pi$—$C_9H_7Mo(CO)_2I]_n$	1956, 1886[c]
$[\pi$—$C_5H_5Mo(CO)_2I]_n$	1960, 1882[c]

[a] in $CHCl_3$ solution; [b] in pentane solution; [c] Nujol mull.

Carbon Monoxide Evolution and Absorption Studies. The method of testing qualitatively for carbon monoxide evolution has been described in a previous paper.[1] The apparatus used for quantitative determination of carbon monoxide evolution or absorption was a Warburg manometer, modified so that a solid sample could be added to a solvent, saturated with CO, under an atmosphere of CO, without opening the system to the external atmosphere.

Equipment· Infra-red spectra were recorded on a Perkin-Elmer 257 spectrophotometer, N.M.R· spectra on a Perkin-Elmer R10 spectrometer and mass spectra on an A.E.I. MS12 spectrometer.

Results

Irradiation of a solution of $[\pi$—$C_9H_7Mo(CO)_3]_2$ in chloroform under an atmosphere of carbon monoxide gave a complex for which analysis suggested the formula π—$C_9H_7Mo(CO)_3Cl$. The correctness of the formula was supported by the close similarity of the infra-red spectrum of the complex in the C–O stretching region to that of the analogous π-cyclopentadienyl complex (see Table II). The parent ion could not be observed in the mass spectrum of the complex (see Table III), which was complicated by the formation of dimeric species caused by thermal decomposition of π—$C_9H_7Mo(CO)_3Cl$ under the conditions necessary to obtain a spectrum. Irradiation of a bromoform solution of $[\pi$—$C_9H_7Mo(CO)_3]_2$ gave the analogous bromo-complex, π—$C_9H_7Mo(CO)_3Br$. In this case, the mass spectrum did show the parent ion.

The reaction of $[\pi$—$C_9H_7Mo(CO)_3]_2$ with iodine had been previously reported by King and Bisnette[3] to give the dicarbonyl complex π—$C_9H_7Mo(CO)_2I$, and this report was backed up by excellent analytical data. Repeating this preparation, we obtained a complex whose melting point (143-4°C), infra-red spectrum (2028, 1958 cm^{-1} in halocarbon mull) and N.M.R. spectrum (2.32 τ, 2.64 τ, 3·68 τ and 4·21 τ in acetone), were virtually identical to those quoted by King and Bisnette.[3] Analytical data on our material were inconclusive, giving results which by themselves would not allow a distinction between the formulations π—$C_9H_7Mo(CO)_2I$ and π—$C_9H_7Mo(CO)_3I$. An X-ray structural determination performed on the complex[4] showed unequivocally that the crystal used consisted of the tricarbonyl species, π—$C_9H_7Mo(CO)_3I$, and other crystals tried gave identical X-ray data. Since there was no evidence from melting-point, infra-red or N.M.R. spectrum to suggest that the preparation had yielded a mixture of two compounds, we conclude that all of the sample consisted of π—$C_9H_7Mo(CO)_3I$. This is supported by the similarity of the infra-red spectrum of the complex to that of π—$C_5H_5Mo(CO)_3I$ (see Table II), and by the observation of the parent ion, albeit at low intensity, in the mass spectrum of the complex (Table III).

All three complexes π—$C_9H_7Mo(CO)_3X$ (X = Cl, Br and I) reacted with phosphorus(III) ligands, L, in accordance with equation (1)

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

The formulation of the products as π—$C_9H_7Mo(CO)_2LX$ is based on analytical data and the similarity of the infra-red spectra (Table II), in the C–O stretching

Table III. Mass Spectra of some π–Indenyl Complexes [a]

(i) π–$C_9H_7Mo(CO)_3X$ (X = Cl, Br and I)

$(C_9H_7)_2Mo_2(CO)_4X_2^+$	
$(C_9H_7)_2Mo_2(CO)_3X_2^+$	$C_9H_7Mo(CO)_3X^+$ [b]
$(C_9H_7)_2Mo_2(CO)_2X_2^+$	$C_9H_7Mo(CO)_2X^+$
$(C_9H_7)_2Mo_2(CO)X_2^+$	$C_9H_7Mo(CO)X^+$
$(C_9H_7)_2Mo_2X_2^+$	$C_9H_7MoX^+$

(ii) π–$C_9H_7Mo(CO)_2LX$

L = $P(OMe)_3$, X = I	L = PBu^n_3, X = I	L = $P(OMe)_3$, X = Br
$C_9H_7Mo(CO)_2LX^+$	$C_9H_7Mo(CO)_2LX^+$	—
$C_9H_7Mo(CO)LX^+$	$C_9H_7Mo(CO)LX^+$	$C_9H_7Mo(CO)LX^+$
$C_9H_7MoLX^+$	$C_9H_7MoLX^+$	$C_9H_7MoLX^+$
$C_9H_7Mo(CO)_2X^+$	—	—
$C_9H_7Mo(CO)X^+$	—	—
$C_9H_7MoX^+$	—	$C_9H_7MoX^+$

[a] All ions showed the normal molybdenum isotopic pattern, with superimposition of other isotopic mixtures. Many ions have been omitted to save space, but a blank in the table means that an ion of this type was not observed. [b] Not for X = Cl.

region, to those of analogous π–cyclopentadienyl complexes. Mass spectra (Table III) of the complexes π–$C_9H_7Mo(CO)_2(P\{OMe\}_3)I$ and π–$C_9H_7Mo(CO)_2(PBu^n_3)I$ were recorded, and showed the presence of the parent ion.

In the case of the reactions of π–$C_9H_7Mo(CO)_3Cl$ and π–$C_9H_7Mo(CO)_3I$ with PPh_3, the gas evolved during the reaction was shown to be carbon monoxide, and quantitative experiments for the latter reaction showed that one mole of carbon monoxide was evolved per mole of π–$C_9H_7Mo(CO)_3I$. (In the absence of added ligand, solutions of π–$C_9H_7Mo(CO)_3I$ under an atmosphere of carbon monoxide neither absorbed nor evolved carbon monoxide).

The reactions of π–$C_9H_7Mo(CO)_3X$ (X = Br, I) with PBu^n_3 yielded, in addition to the « normal » product π–$C_9H_7Mo(CO)_2(PBu^n_3)X$, small quantities of « unexpected » products, *fac*–$Mo(CO)_3(PBu^n_3)_3$ and *cis*–$Mo(CO)_4(PBu^n_3)_2$. The analogous reaction of π–$C_5H_5Mo(CO)_3Cl$ has been discussed in a previous paper,[2] and — assuming that the reaction of the indenyl complexes follows the same course — we can write equations (2) and (3) for the formation of the « unexpected » products, where the carbon monoxide for reaction (3) comes from the « normal » reaction (1).

$$\pi\text{–}C_9H_7Mo(CO)_3X + 4PBu^n_3 \longrightarrow [C_9H_7PBu^n_3]^+ + X^- + Mo(CO)_3(PBu^n_3)_3 \quad (2)$$

$$Mo(CO)_3(PBu^n_3)_3 + CO \longrightarrow Mo(CO)_4(PBu^n_3)_2 + PBu^n_3 \quad (3)$$

All three complexes π–$C_9H_7Mo(CO)_3X$ (X = Cl, Br and I) were affected by prolonged heating at 100°C under high vacuum. After a day, none of the starting material remained and, although in every case some decomposition to non-carbonyl-containing compounds had occurred, nujol mull infra-red spectra of the residues (see Table II) showed the presence of a new carbonyl-containing compound. The ratio of new compound to decomposition products was most favourable for the chloro-complex, and least favourable for the iodo-complex.

An apparently similar compound could be obtained from π–$C_5H_5Mo(CO)_3I$ by the same method or — in considerably better yield — as a precipitate on irradiating π–$C_5H_5Mo(CO)_3I$ in hexane. The product was slightly soluble in hexane, and in the absence of irradiation the infra-red spectrum of the hexane solution changed fairly quickly, with accompanying decomposition, from that of the new complex to that of π–$C_5H_5Mo(CO)_3I$. A similar but much faster change, again with accompanying decomposition, occurred on treating the analogous π–indenyl compounds with hexane or chloroform.

When the new compounds were treated with hexane saturated with carbon monoxide, under an atmosphere of carbon monoxide, there was very little decomposition, and nearly quantitative conversion back to the tricarbonyl complexes, π–$C_9H_7Mo(CO)_3X$ and π–$C_5H_5Mo(CO)_3I$. Quantitative experiments showed that an amount of carbon monoxide varying between 0.85 and 0.95 moles per molybdenum atom was being taken up during these reactions. We believe that the new complexes should be formulated as $[\pi\text{–}C_9H_7Mo(CO)_2X]_n$ and $[\pi\text{–}C_5H_5Mo(CO)_2I]_n$. Such complexes would take up one mole of carbon monoxide per molybdenum atom, but the inevitable presence of impurities (caused by decomposition during the original preparation) would account for the slightly lower figures actually obtained. In solution in the absence of added carbon monoxide, we assume that decomposition of some of the dicarbonyl complex to non-carbonyl-containing materials liberates carbon monoxide, which then reacts with the remainder of the dicarbonyl complex to give the observed partial conversion to tricarbonyl complex.

Purification of the dicarbonyl complexes proved to be impossible. Aanlytical data for the complex formed with the least decomposition, $[\pi\text{–}C_9H_7Mo(CO)_2Cl]_n$, were close enough to be compatible with this formulation, but not to give any conclusive support for it. The formulation of these compounds as dicarbonyl complexes is supported by the fact that all react with triphenylphosphine to give complexes π–$C_9H_7Mo(CO)_2(PPh_3)X$ and π–$C_5H_5Mo(CO)_2PPh_3X$ without evolution of carbon monoxide. The rates of these reactions are much greater than those of the tricarbonyl complexes with triphenylphosphine:

Table IV. N.M.R. Spectra[a] for Protons A, A′ and B (see Figure) in some π-Indenyl Complexes.

	A	A′	B
π–$C_9H_7Mo(CO)_3Cl$	3.81(2)[d]		4.18(1)[t]
π–$C_9H_7Mo(CO)_3Br$	3.72(2)[d]		4.18(1)[t]
π–$C_9H_7Mo(CO)_3I$	3.68(2)[d]		4.21(1)[t]
π–$C_9H_7Mo(CO)_2(PPh_3)Cl$	3.74(1)[b]	4.62(1)[b]	4.70(1)[t]
π–$C_9H_7Mo(CO)_2(P\{OMe\}_3)Cl$	3.96(1)[b]	4.22(1)[b]	4.74(1)[t]
π–$C_9H_7Mo(CO)_2(PPh_3)Br$	3.84(1)[b]	4.59(1)[b]	4.81(1)[t]
π–$C_9H_7Mo(CO)_2(PBu^n_3)Br$	3.81(1)[b]	4.46(1)[b]	4.65(1)[t]
π–$C_9H_7Mo(CO)_2(P\{OMe\}_3)Br$	4.06(1)[b]	4.26(1)[b]	4.82(1)[t]

[a] τ values in CD_3COCD_3 solution. Intensities are given in parentheses. [b] Broad band. [d] Doublet. [t] Triplet.

for example, the reaction of π–$C_5H_5Mo(CO)_3I$ with triphenylphosphine is immeasurably slow in hexane at 25°C, while that of $[\pi$–$C_5H_5Mo(CO)_2I]_n$ under the same conditions is complete within a few hours.

Discussion

The structure[4] of π–$C_9H_7Mo(CO)_3I$ is essentially a square-based pyramid, with the indenyl ligand as the apex and the three carbonyl ligands and the iodide ligand forming the square base. In the solid state, the iodide ligand does not lie on the plane of symmetry (dotted line in Figure) through the indenyl ligand, but in solution in d^6-acetone the protons A and A′ (see Figure) are aparently equivalent (see N.M.R. spectra, Table IV). Either the structure has become symmetrical or, more likely, the indenyl ligand is in rapid motion relative to the remaining ligands (as the π-cyclopentadienyl ligand is believed to be in most of its complexes).

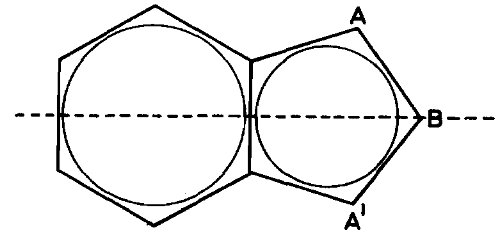

Figure 1. Notation for Protons on Five-Membered Ring of π–Indenyl Ligand.

Assuming that the stereochemistry of the complexes π–$C_9H_7Mo(CO)_2LX$ is similar to that of π–$C_9H_7Mo(CO)_3I$, pairs of isomers can be expected, with the ligands L and X either « *cis* » or « *trans* » in the square base of the pyramid. If the indenyl ligand can still move freely, the N.M.R. spectra of such complexes should allow a distinction between *cis*- and *trans*-stereochemistry in a way which is not possible for complexes π–$C_5H_5Mo(CO)_2LX$ (except in special cases[5] such as L = PMe_2Ph). *Trans*-stereochemistry will make the protons A and A′ equivalent, while a *cis*-arrangement must make them non-equivalent.

The N.M.R. spectra of these complexes (Table IV) show two resonances for A and A′, much too far apart to be the result of coupling to the ^{31}P nucleus in the ligand L. Only one resonance was observed for proton B, and all three resonances integrated correctly for a single proton, showing the presence of a single isomer only. This means that either the complexes all have *cis*-stereochemistry, or they have *trans*-stereochemistry with the indenyl ligand fixed in an unsymmetrical position. The assumption of *cis*-stereochemistry is in agreement with the failure to observe coupling of the protons A, A′ and B to the ^{31}P nucleus in L, which has proved to be a reliable means of distinguishing *cis*–π–$C_5H_5Mo(CO)_2$-LX complexes from their *trans*-isomers.[6]

The structure of the complexes $[\pi$–$C_9H_7Mo(CO)_2X]_n$ (X = Cl, Br and I) is uncertain. Molecular weight and dipole moment determinations could not be performed since the complexes decomposed in all solvents in which they were soluble. If n = 1, the complexes do not have an inert gas configuration. Such a configuration can be achieved if n = 2, either by bridging through halogen or by a direct metal-metal bond.

The mass spectra (Table III) of the complexes π–$C_9H_7Mo(CO)_3X$ were obtained under conditions very similar to those used to prepare the complexes $[\pi$–$C_9H_7Mo(CO)_2X]_n$. It is most intriguing to note that a series of ions $[(\pi$–$C_9H_7)_2Mo_2(CO)_nX_2]^+$, where n = 4, 3, 2, 1 and 0, is clearly visible for each complex albeit at low intensity, with the characteristic isotopic distribution pattern for Mo_2 noticeable in each case. This appears to be strong evidence that the complexes $[\pi$–$C_9H_7Mo(CO)_2X]_n$ are dimeric, and are being formed during the volatization of the samples of π–$C_9H_7Mo(CO)_3X$ in the spectrometer.

In view of the similarity of the infra-red spectra of the complexes $[\pi$–$C_9H_7Mo(CO)_2X]_2$ to those of complexes π–$C_9H_7Mo(CO)_2XL$, a halogen-bridged structure seems likely. A similar resemblance is noticeable[7] between the spectra for complexes *cis*–$Re(CO)_4LX$ and the halogen-bridged complexes $[Re(CO)_4X]_2$.

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