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**OXIDATION OF η^6 -ARENE COMPLEXES OF GROUP VI
METALS. III (*). DI-IODINE-CATALYSED CARBONYLATION
OF MOLYBDENUM(0)- η^6 -ARENE COMPLEXES TO $\text{Mo}(\text{CO})_6$
AND EXPERIMENTAL EVIDENCE OF AN INNER-SPHERE
ELECTRON-TRANSFER REACTION BETWEEN CENTRES OF
MOLYBDENUM(II) AND MOLYBDENUM(0) (**)**

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Summary – Carbonylation of $\text{Mo}(\text{CO})_3(\eta^6\text{-arene})$ has been found to be catalysed by I_2 , or by $[\text{MoI}(\text{CO})_3(\eta^6\text{-arene})][\text{Mo}_2\text{I}_5(\text{CO})_6]$ or by $\text{Mo}_2\text{I}_4(\text{CO})_8$. Earlier papers in this series have shown the latter molybdenum(II) complexes to be the products of $\text{Mo}(\text{CO})_3(\eta^6\text{-arene})$ oxidation by I_2 in the absence or in the presence of carbon monoxide, respectively. The rate of carbonylation to $\text{Mo}(\text{CO})_6$ decreases with the methyl substitution on the carbocyclic ligand. A fast process between $\text{Mo}(\text{CO})_3(\eta^6\text{-arene})$ and $[\text{MoI}(\text{CO})_3(\eta^6\text{-arene}')]\text{X}$ ($\text{X} = \text{BPh}_4$, $[\text{Mo}_2\text{I}_5(\text{CO})_6]$) leading to $\text{Mo}(\text{CO})_3(\eta^6\text{-arene}')$ and $[\text{MoI}(\text{CO})_3(\eta^6\text{-arene})]\text{X}$ has been observed in dichloromethane solution. This is believed to be in fact an inner-sphere iodide transfer process, *i.e.* an $\text{Mo}(0)$ - $\text{Mo}(\text{II})$ two-electron transfer simulating an arene exchange. The $[\text{MoI}(\text{CO})_3(\eta^6\text{-arene})]^+$ cation is believed to play an important role in both the apparent arene exchange and the carbonylation process via an iodide-bridged mixed-valence common intermediate.

(*) For Part II, see preceding paper.

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Molybdenum(0) arene complexes, $\text{Mo(CO)}_3(\eta^6\text{-arene})$, undergo arene displacement by a number of ligands L, such as PR_3 ,^{1a-c} P(OR)_3 ,^{1d} MeCN,^{1e} amine,^{1f} tetrahydrofuran (THF),^{1g} acetone^{1g} to produce the corresponding $\text{Mo(CO)}_3\text{L}_3$ under milder conditions than usually required by the corresponding tungsten and chromium systems. The molybdenum(0)-arene complexes are also known to be easily oxidised, the oxidation products being isolable molybdenum(II) tricarbonyl complexes in certain cases.² Di-iodine oxidation of $\text{Mo(CO)}_3(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)$ was reported to yield the ionic³ $[\text{MoI(CO)}_3(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)]\text{I}$. No chromium analogue of such product is known, the oxidation of $\text{Cr(CO)}_3(\eta^6\text{-arene})$ generally leading to chromium(III) species not containing coordinated carbon monoxide. A comparative study of the electrochemical oxidation of $\text{M(CO)}_3(\eta^6\text{-arene})$, $\text{M} = \text{Cr, Mo, W}$, has recently been carried out,⁴ the more relevant result for our study being that the tungsten systems, due to the availability of a seventh coordination position, rapidly interacts with the solvent after the one-electron process has occurred, leading to solvent-dependent oxidations. The chromium system, on the other hand, undergoes a one-electron oxidation process which does not depend on the nature of the solvent; this is followed by loss of the ligands and further oxidation to chromium(III), which is the ultimate product. The initial one-electron process approaches reversibility for the chromium derivatives containing highly crowded arene groups.⁴

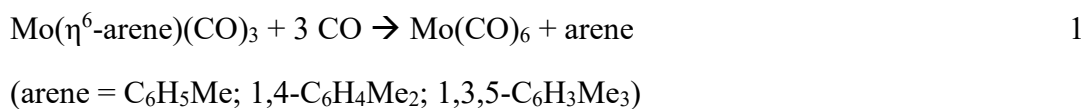
The oxidation of metal carbonyl derivatives has recently attracted considerable interest in view of the electron-transfer catalysis (ETC) observed in a number of processes, including ligand displacement reactions.^{5,6} This means that a fast ligand substitution occurs following a chemical⁵ or electrochemical⁶ one-electron oxidation. A report concerning the di-iodine-catalysed arene exchange in $\text{Cr(CO)}_3(\eta^6\text{-arene})$ has recently appeared.^{7a}

In attempts to oxidise $\text{Mo(CO)}_3(\eta^6\text{-arene})$ complexes aimed at detecting carbonyl compounds of intermediate oxidation states, which required the use of sub-stoichiometric amounts of the oxidising agent, we found that I_2 catalyses the carbonylation of the tricarbonyl complexes of molybdenum(0) to Mo(CO)_6 . Such an effect attracted our interest because of: a) the above-mentioned relationship between oxidation and ligand substitution reactions (ETC), and, b) the possible use of this process as a non-oxidative method for releasing the arene ligand after ring-substitution reactions.^{7b} For these reasons, we started an extensive study of the catalytic process.

The stoichiometric oxidations of $\text{Mo(CO)}_3(\eta^6\text{-arene})$ by I_2 had been the subject of earlier papers.^{8,9} We report here on the carbonylation of the arene-molybdenum(0) complexes catalysed by I_2 and by a number of molybdenum(II) complexes. An apparent arene exchange process, whose true nature is probably closely related to the mechanism of the catalytic carbonylation, is also presented.

RESULTS AND DISCUSSION

When a solution of $\text{Mo(CO)}_3(\eta^6\text{-arene})$, arene = $\text{C}_6\text{H}_5\text{Me}$; 1,4- $\text{C}_6\text{H}_4\text{Me}_2$; 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$, was treated with CO at atmospheric pressure in the same arene as solvent, a slow absorption of CO was observed at room temperature. However, addition of a relatively small amount of I_2 increased the rate of carbonylation enormously. CO was found to be absorbed up to a CO/Mo ratio of about 3, affording solutions whose IR spectrum showed Mo(CO)_6 as the only carbonyl species present, see equation 1. The rate of arene displacement depended on the arene itself, being smaller as the methyl substitution on the ring increased (see figure 1). This is in agreement with kinetic studies on arene displacement reactions in $\text{Mo(CO)}_3(\eta^6\text{-arene})$ by ligands such as P(OMe)_3 ,^{1d} PCl_3 , PCl_2Ph , P^nBu_3 ,^{1a} and can be explained with a stronger arene-metal bond as methyl substitution increases.¹⁰ Attempts were made to measure the kinetics of our iodine-catalysed carbonylation reaction but the rate data did not correspond to any simple kinetic law.



A similar catalytic effect operates for the arene displacement by CO in the corresponding tungsten tricarbonyl compounds to form W(CO)_6 . The catalysed uptake of CO was too slow in this case and discouraged any further investigation.

The chromium(0)-arene complexes, on the other hand, did not absorb any CO in the presence of I_2 ; on the contrary, an amount of CO strictly corresponding to the di-iodine introduced was evolved, in agreement with the stoichiometry of equation 2.¹¹

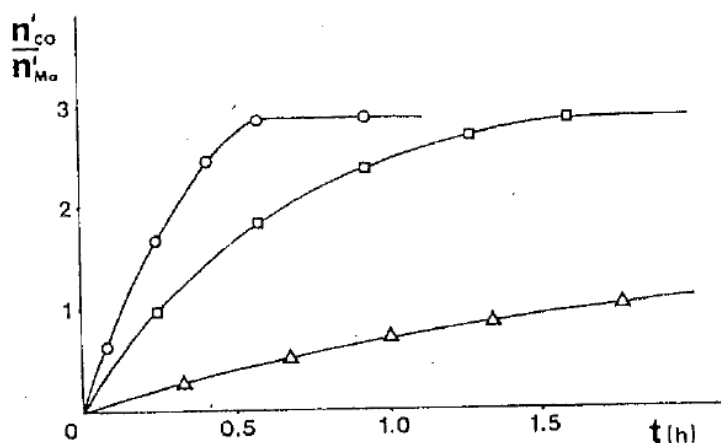
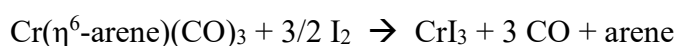


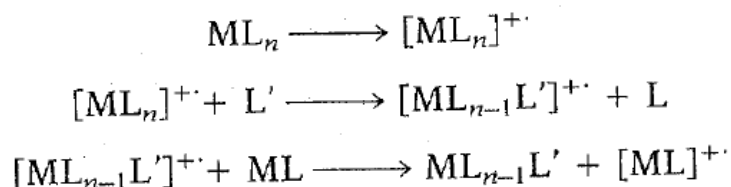
Fig. 1 - Di-iodine catalysed carbonylation of $\text{Mo}(\text{CO})_3(\eta^6\text{-arene})$ as a function of the arene. For details concerning the $n'_{\text{CO}}/n'_{\text{Mo(0)}}$ molar ratio in ordinates, see text. The solvent is the neat parent aromatic hydrocarbon. Experimental conditions: $[\text{Mo(0)}]$, $5.44 \times 10^{-2} \text{ M}$; $[\text{I}_2]$, $2.52 \times 10^{-3} \text{ M}$; temperature: $24.5 \pm 0.1^\circ \text{C}$; $p_{\text{CO}} + p_{\text{solvent}}$: atmospheric pressure. Legend for the arene: \circ , $\text{C}_5\text{H}_5\text{Me}$; \square , $1,4\text{-C}_5\text{H}_4\text{Me}_2$; \triangle , $1,3,5\text{-C}_6\text{H}_3\text{Me}_3$.



2

A report exists in the literature on the catalytic effect of I_2 on the arene exchange in $\text{Cr}(\eta^6\text{-arene})(\text{CO})_3$.⁷ This phenomenon has been interpreted⁷ as an electron-transfer catalysis, see scheme 1. On the other hand, although the arene displacement by CO is expected to follow the same route as the arene exchange reaction, only oxidation to CrI_3 was observed with the chromium(0) complexes and no trace of $\text{Cr}(\text{CO})_6$ was found spectroscopically.

SCHEME 1



Assuming that the formation of the 17-electron $[\text{Cr}(\eta^6\text{-arene})(\text{CO})_3]^+$ cation, resulting from the one-electron oxidation by I_2 occurs in both cases, we attribute the different behaviour to a concentration effect. In the arene exchange reported by Harrison⁷ the incoming arene is present in

great excess being used as solvent (*e.g.*, the concentration of 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$ in the neat liquid is *ca.* 8 M). Thus, the proposed 17-electron intermediate could undergo arene exchange at a rate comparable to that of its irreversible further oxidation. As a matter of fact, as reported by Harrison,⁷ the catalyst deactivates with time, the catalytic activity being restored by addition of di-iodine. In the displacement reaction by CO, the concentration of the latter reagent is much smaller (about 7×10^{-3} M in most of the organic solvents¹²) and we can therefore expect that the competing oxidation of the 17-electron intermediate to CrI_3 would become predominant.

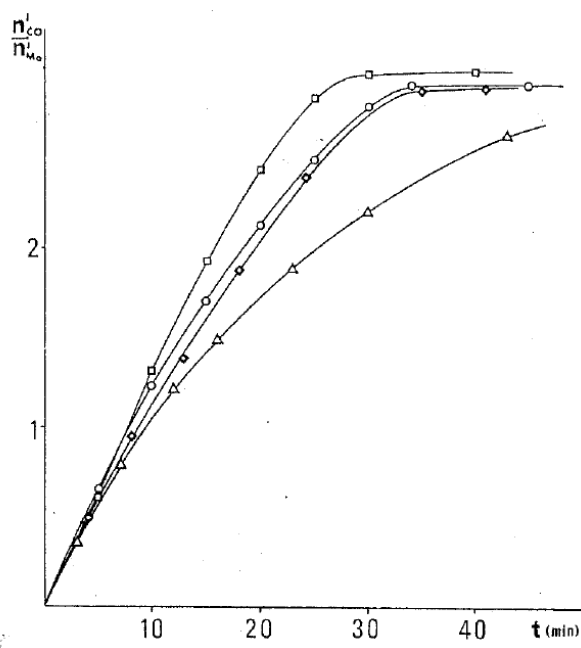


Fig. 2 - Comparative effects of various catalysts-on the carbonylation of $\text{Mo(CO)}_3(\eta^6\text{-C}_6\text{H}_5\text{Me})$ to Mo(CO)_6 . The $n'_{\text{CO}}/n'_{\text{Mo(0)}}$ molar ratio in ordinates has the same meaning as in figure 1. Solvent: toluene; temperature: 24.5 ± 0.1 °C; $p_{\text{CO}} + p_{\text{solvent}}$: atmospheric pressure. Concentrations used: (O) $[\text{Mo(0)}]$, 5.44×10^{-2} M, $[\text{I}_2]$, 2.52×10^{-3} M; (□) $[\text{Mo(0)}]$, 5.21×10^{-2} M, **[1]**, 8.60×10^{-4} M; (Δ) $[\text{Mo(0)}]$, 5.31×10^{-2} M; $[\text{Mo}_2\text{I}_4(\text{CO})_8]$, 1.25×10^{-3} M; (◇) $[\text{Mo(0)}]$, 5.14×10^{-2} M, **[3]**, 9.80×10^{-4} M.

By considering the dramatic difference in behaviour between chromium and molybdenum in both the carbonylation reaction and the previously-mentioned electrochemical experiment,⁴ we propose that the here reported I_2 -catalysed carbonylation of molybdenum(0) complexes does not proceed via an ETC mechanism and we propose an alternative route. Our considerations are based on a systematic study of the products of the stoichiometric oxidations of molybdenum(0) complexes by

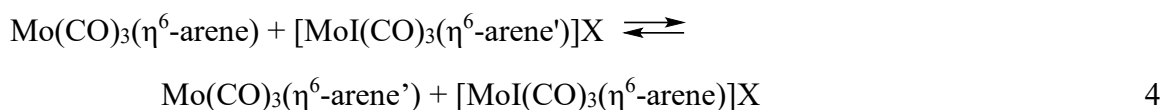
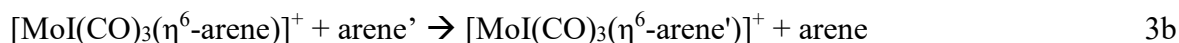
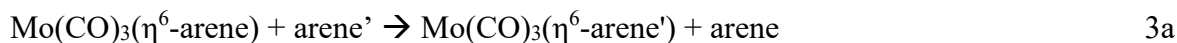
di-iodine. Earlier, compounds were isolated of composition⁸ $[\text{MoI}(\eta^6\text{-arene})(\text{CO})_3][\text{Mo}_2\text{I}_5(\text{CO})_6]$ (arene = $\text{C}_6\text{H}_5\text{Me}$, **1**; 1,4- $\text{C}_6\text{H}_4\text{Me}_2$, **2**; 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$, **3**). When compound **1** was introduced into the $\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{CO})_3/\text{CO}$ system, a catalytic effect was noted, see figure 2, corresponding to that observed with the equivalent amount of I_2 . A similar effect was observed when the equivalent amount of iodine was introduced under the form of compound **3**.

In order to get further insight into the mechanism of the catalytic carbonylation, we studied the behaviour of compounds **1** - **3** under CO: they were found to form the known¹³ $\text{Mo}_2\text{I}_4(\text{CO})_8$, **4**, selectively. This proved to be the best method so far known for the preparation of **4**.⁹ A catalytic effect was observed with **4**, see figure 2. Furthermore, the stoichiometric reaction of **4** with the molybdenum(0)-arene complex led to the slow formation of the known¹⁴ $\text{Mo}_2\text{I}_2(\text{CO})_8$.

Some by-products were also formed which could not be identified in most cases. However, in the reaction with $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)$, the known⁸ complex $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)][\text{MoI}_3(\text{CO})_4]$ was characterised.

$\text{Mo}_2\text{I}_2(\text{CO})_8$ was detected spectroscopically at the end of the carbonylations carried out by using either I_2 or complexes **1** - **4** as catalysts. We therefore conclude that if $\text{Mo}_2\text{I}_4(\text{CO})_8$ is present at any stage of the catalytic carbonylation, it is rapidly converted to products other than $\text{Mo}_2\text{I}_2(\text{CO})_8$, which we could otherwise detect spectroscopically.

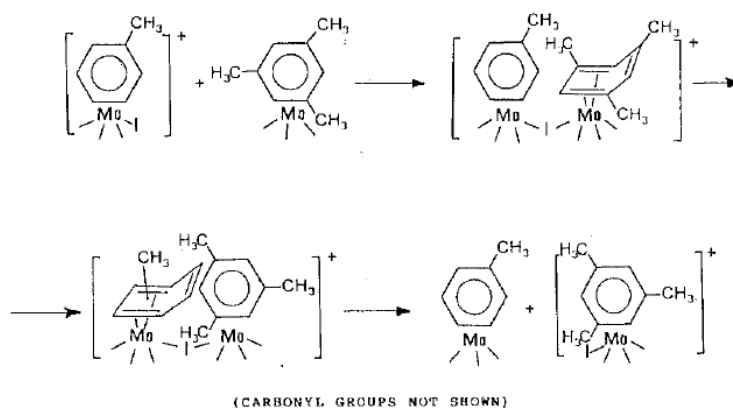
Further evidence that a mechanism different from that suggested⁷ in the case of $\text{Cr}(\text{CO})_3(\eta^6\text{-arene})$ is operating with the molybdenum(0) complexes, comes from the observation that no accelerated arene exchange was found upon addition of small amounts of di-iodine to the molybdenum(0)-arene complex in neat arene' as solvent, see equation 3a. Moreover, the complexes $[\text{MoI}(\text{CO})_3(\eta^6\text{-arene})][\text{Mo}_2\text{I}_5(\text{CO})_6]$ were found to be stable with respect to arene exchange with arene' used as medium (eq. 3b). On the contrary, a fast arene exchange was found to occur when equimolar amounts of molybdenum(0)-arene and molybdenum(II)-arene' complexes were mixed in dichloromethane as solvent, see eq. 4. The exchange was a rather slow process when carried out in *n*-heptane as medium [the molybdenum(II) complex is only sparingly soluble], but it became nearly immediate in dichloromethane. The exchange was found to be shifted towards the formation of the more methyl-substituted molybdenum(II) complex.



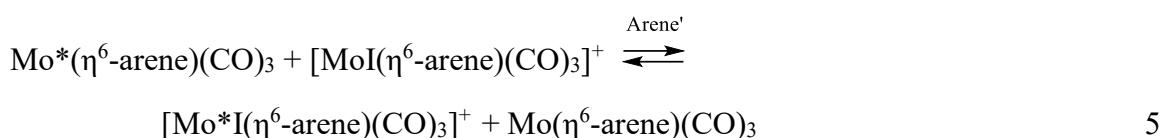
Arene	Arene'	X	Solvent
1,3,5-C ₆ H ₃ Me ₃	C ₆ H ₅ Me	[Mo ₂ I ₅ (CO) ₆] ⁻	<i>n</i> -Heptane
1,3,5-C ₆ H ₃ Me ₃	C ₆ H ₅ Me	BPh ₄ ⁻	CH ₂ Cl ₂
1,3,5-C ₆ H ₃ Me ₃	C ₆ H ₅ Me	BPh ₄ ⁻	CH ₂ Cl ₂

Thus, while both the molybdenum(0)- and the molybdenum(II)-arene complexes are in slow equilibrium with free arene', a fast arene exchange was found to occur between the molybdenum(0) and the molybdenum(II) containing the precoordinated arene groups to be exchanged. This observation led us to conclude that we are actually dealing with an *apparent* arene exchange and that the arene ligands never leave the molybdenum centre to which they were originally bonded. We therefore suggest the mechanism shown in scheme 2, where the specific case of arene (1,3,5-C₆H₃Me₃) and arene' (C₆H₅Me) is illustrated. We would therefore deal with a two-electron transfer process triggered by an iodide transfer from a molybdenum centre to the other one, simulating an arene exchange. This mechanism is similar to the well-known¹⁵ inner-sphere redox reactions encountered in classical coordination chemistry. The latter are generally one-electron transfer processes. An inner-sphere two-electron redox process has been postulated¹⁶ for the chloride exchange in [Pt(en)₂Cl₂]²⁺ catalysed by [Pt(en)₂]²⁺.

SCHEME 2

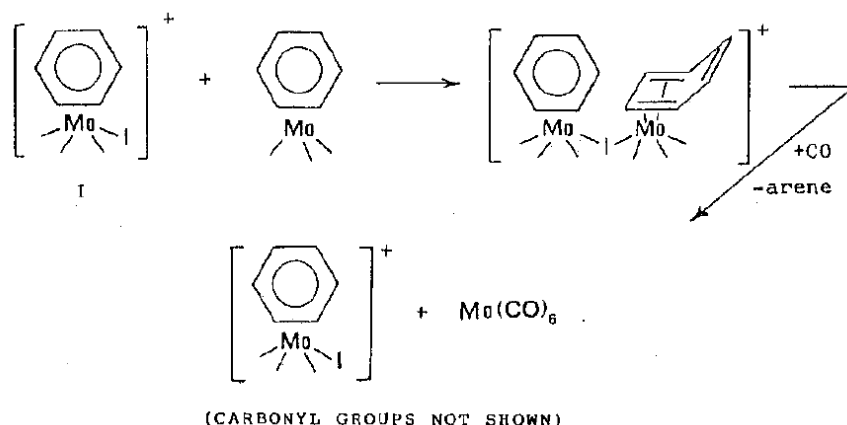


We can now explain the absence of a catalytic effect of I₂ on the Mo(CO)₃(η⁶-arene)/arene' exchange. Di-iodine in fact reacts⁸ with the molybdenum(0) complex to give the molybdenum(II) derivatives **1-3**. The latter would then react with the excess of the molybdenum(0) complex still present in solution giving rise to no useful exchange reaction since both reactants have the same arene as a ligand, see equation 5.



On the basis of the molybdenum(II) chemistry which has been discussed in this paper and in earlier ones^{8,9} we can tentatively suggest a mechanism for the I₂-catalysed carbonylation of molybdenum(0)-arene complexes. An interesting literature datum relevant to this discussion is the observation¹⁷ that the M(η⁶-arene)(CO)₃, M = Cr, Mo, W, react with halide to afford the ionic [M₂X₃(CO)₆]³⁻. The reaction was reported to be immediate at room temperature in the (M = Mo, X = I) case. This shows the arene group attached to molybdenum(0) to be labile towards substitution by a monodentate ligand such as I⁻, the reaction probably involving η⁴ or η² carbocyclic intermediates due to the increased electron counting around the central metal atom resulting from I⁻ coordination. We can therefore suggest that the cationic molybdenum(II) species indicated as **I** in scheme 3 [formed by I₂ reaction on the molybdenum(0) complex⁸] can attack the molybdenum(0)-arene complex to form the iodide-bridged molybdenum(0)-molybdenum(II) species, thus leading to a labilisation of the arene ligand. It should be noted that the dinuclear intermediate suggested in scheme 3 is the same as that suggested to be involved in the redox process (apparent arene exchange) of equation 4. Our suggestion is therefore that the effect of I₂ on the carbonylation of Mo(CO)₃(η⁶-arene) is to produce molybdenum(II) compounds containing terminal iodide ligand which can act as catalysts via the formation of iodide-bridged mixed-valence intermediates.

SCHEME 3



Arene labilisation by monodentate ligands was further confirmed by the following experiments. The molybdenum(0) complex $\text{Mo(CO)}_3(\eta^6\text{-C}_6\text{H}_5\text{Me})$ afforded Mo(CO)_6 at atmospheric pressure of CO when dissolved in EtOH. Furthermore, when the toluene-molybdenum(0) compound was treated with NBu_4I in dichloromethane and the resulting¹⁷ $[\text{Mo}_2\text{I}_3(\text{CO})_6]^{3-}$ interacted with CO, the substantially quantitative formation of the known¹⁸ $[\text{MoI(CO)}_5]^-$ was observed spectroscopically.

On the basis of the present results it appears that, contrary to what has been found for the $\text{Cr(CO)}_3(\eta^6\text{-arene})$ systems,⁷ di-iodine does not operate with molybdenum via an ETC type of mechanism. Thus, molybdenum(0) - and presumably tungsten(0) - arene carbonyl complexes differ considerably from the corresponding chromium(0) systems for both their electrochemical and chemical properties.

EXPERIMENTAL

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified dinitrogen or argon. Solvents were carefully dried prior to use by conventional methods. IR spectra were measured with Perkin-Elmer Z83 or 283B instruments equipped with grating; each solution spectrum in the carbonyl stretching region was recorded on an expanded abscissa scale and calibrated with both CO and $\text{H}_2\text{O}_{(\text{g})}$, the wavenumber values being therefore believed to be accurate to $\pm 1 \text{ cm}^{-1}$. The following $\eta^6\text{-arene}$ complexes were prepared according to published procedures: $\text{Mo(CO)}_3(\eta^6\text{-arene})$ (arene = $\text{C}_6\text{H}_5\text{Me}^{19}$; $1,3,5\text{-C}_6\text{H}_3\text{Me}_3^{1d}$; C_6Me_6^8), $[\text{MoI(CO)}_3(\eta^6\text{-arene})][\text{Mo}_2\text{I}_5(\text{CO})_6]$ (arene as above⁸), $[\text{MoI(CO)}_3(\eta^6\text{-C}_6\text{Me}_6)]\text{X}$ ($\text{X} = \text{I}_3, \text{BPh}_4$)⁸. $[\text{MoI(CO)}_3(\eta^6\text{-$

$\text{C}_6\text{H}_5\text{Me})\text{]BPh}_4$ was prepared following the procedure reported⁸ for its C_6Me_6 analogue, namely by the metathetical reaction of the corresponding tri-iodide with BPh_4^- in dichloromethane as solvent; since this compound, and the corresponding tri-iodide, unlike the C_6Me_6 derivative, have limited stability at room temperature either as solids or in solution, particular care had to be taken during the synthesis. The tri-iodide was generated *in situ* from $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_5\text{Me})$ (0.66 g; 2.42 mmol) and I_2 (1.24 g; 4.88 mmol) in 50 cm⁴ of dichloromethane. The resulting mixture was immediately treated with NBu_4BPh_4 (1.53 g; 2.72 mmol), which gave a red microcrystalline precipitate. This was quickly filtered off, washed with dichloromethane (2 x 10 cm³) and dried in vacuo (0.26 g; 15% yield). Satisfactory elemental analyses and clean IR spectra in solution could not be obtained due to rapid decomposition, but the identity of the product as $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_5\text{Me})]\text{BPh}_4$ is suggested by the analogy of its synthesis with that of the corresponding C_6Me_6 derivative,⁸ and by its reactions with the molybdenum(0) complexes, *vide infra*.

CATALYSED CARBONYLATION REACTIONS OF $\text{Mo}(\text{CO})_3(\eta^6\text{-ARENE})$, ARENE = $\text{C}_6\text{H}_5\text{Me}$; 1,4- $\text{C}_6\text{H}_4\text{Me}_2$; 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$

These reactions were carried out in a gasvolumetric burette equipped with a thermostat, as already described.¹² A known amount of the molybdenum(0) complex was introduced into the reactor together with a known volume of the parent arene as solvent and the system was saturated with CO at atmospheric pressure. A control experiment showed that the uncatalysed carbonylation of the molybdenum(0) complex proceeded at a negligible rate. A weighed amount of the catalyst was then introduced, sealed in a thin-walled flask, under a stream of CO. After the entire apparatus had been allowed to attain thermal equilibrium, the sealed flask was crushed with a magnetically stirred bar to start the reaction. The rate of stirring was such that the CO diffusion into the solution was not rate controlling. The temperature remained constant to ± 0.1 °C during each run. Volume readings were treated by applying the ideal gas law, the CO partial pressure being obtained from the atmospheric pressure, as read from the barometer, after correction for the vapour pressure of the solvent. The resulting data were converted to CO/Mo(0) molar ratios, $n'_{\text{CO}}/n'_{\text{Mo(0)}}$: the observed moles of molybdenum(0) and CO, $n_{\text{Mo(0)}}$ and n_{CO} , were corrected for the stoichiometric reactions occurring with the catalyst.^{8,9} In the I_2 -catalysed reaction, for example, an amount of molybdenum(0) equivalent

to the I₂ introduced is consumed to afford⁸ the complex [MoI(CO)₃(η⁶-arene)][Mo₂I₅(CO)₆]. The latter then reacts with CO producing⁹ Mo₂I₄(CO)₈, thus consuming one mole of CO *per* mole of molybdenum(0). The final data were therefore obtained according to the following equation 6. Equations 7 and 8, respectively, were used to obtain the CO/Mo molar ratio, when the catalysts were [MoI(CO)₃(η⁶-arene)][Mo₂I₅(CO)₆] and Mo₂I₄(CO)₈. In all cases the approximation was made to neglect the volume of CO pertaining to the equilibrium between Mo₂I₄(CO)₈ and, presumably,⁹ Mo₂I₄(CO)₇. The final data were plotted vs. time as shown in figures 1 and 2.

$$\frac{n'_{\text{CO}}}{n'_{\text{Mo(0)}}} = \frac{n_{\text{CO}} - n_{\text{cat}}}{n_{\text{Mo}} - n_{\text{cat}}} \quad 6$$

$$\frac{n'_{\text{CO}}}{n'_{\text{Mo(0)}}} = \frac{n_{\text{CO}} - 3n_{\text{cat}}}{n_{\text{Mo(0)}}} \quad 7$$

$$\frac{n'_{\text{CO}}}{n'_{\text{Mo(0)}}} = \frac{n_{\text{CO}}}{n_{\text{Mo(0)}}} \quad 8$$

APPARENT ARENE EXCHANGE REACTIONS

A) [MoI(CO)₃(η⁶-C₆H₅Me)][Mo₂I₅(CO)₆] and Mo(CO)₃(η⁶-1,3,5-C₆H₃Me₃) in *n*-heptane - The molybdenum(II) compound⁸ (0.080 g; 0.057 mmol) and the molybdenum(0) derivative (0.16 g; 0.060 mmol) were suspended in *n*-heptane (4 cm³) and stirred at room temperature. The reaction was monitored by IR in the carbonyl stretching region on the soluble compounds: the bands of starting mesitylene complex (partially dissolved) at 1975 and 1903 cm⁻¹ did not change their intensity, while two new bands at 1983 and 1909 cm⁻¹ [corresponding to Mo(CO)₃(η⁶-C₆H₅Me)] increased in intensity over a period of 5 h. The solid was filtered, washed accurately with *n*-heptane and dried *in vacuo*. Its IR spectrum (Nujol) confirmed the presence of [MoI(CO)₃(η⁶-C₆H₃Me₃)][Mo₂I₅(CO)₆], by comparison with an authentic sample.⁸

B) [MoI(CO)₃(η⁶-C₆H₅Me)]BPh₄ and Mo(CO)₃(η⁶-1,3,5-C₆H₄Me₃) in *n*-heptane - The tetraphenylborato complex (0.039 g; 0.054 mmol) and 0.011 g (0.037 mmol) of the molybdenum(0) complex were stirred in *n*-heptane (5 cm³) at room temperature and the reaction was monitored as described above. Again, as for the corresponding reaction with the [Mo₂I₅(CO)₆]⁻ derivative, the

bands of the molybdenum(0) complex at 1983 and 1909 cm^{-1} increased with time, the bands of the starting molybdenum(0) complex being still present after 2 days.

C) $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_5\text{Me})]\text{BPh}_4$ and $\text{Mo}(\text{CO})_3(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)$ in CH_2Cl_2 - The molybdenum(0) complex (0.015 g; 0.050 mmol) was dissolved in dichloromethane (5 cm^3). The resulting yellow solution had IR bands at 1960 and 1875 cm^{-1} . To this was added the freshly prepared tetraphenylborato complex (0.023 g; 0.032 mmol). Soon after mixing, the solution showed bands at 2073m, 2018m, 1966s and 1879s cm^{-1} . The latter two bands were slightly asymmetric, showing shoulders on the low-frequency side. The bands at 1966 and 1879 cm^{-1} correspond to $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_5\text{Me})$, by comparison with an authentic sample, the two shoulders being due to unreacted molybdenum(0) complex. The bands at 2073 and 2018 cm^{-1} are due⁸ to the $[\text{MoI}(\text{CO})_3(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)]^+$ cation.

D) $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_5\text{Me})]\text{BPh}_4$ and $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)$ in CH_2Cl_2 - The molybdenum(0) complex (0.015 g; 0.044 mmol) was dissolved in dichloromethane (5 cm^3), the resulting solution showing bands at 1945s and 1855s cm^{-1} . After addition of the tetraphenylborato complex (0.018 g; 0.025 mmol), the solution had bands at 2067m, 2011m, 1967s, 1945m, 1880s,br and about 1850sh cm^{-1} ; unreacted molybdenum(0) complex, 1945 and 1850 cm^{-1} , and $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)]^+$, 2067 and 2011 cm^{-1} . The spectrum did not change with time. After about 0.5 h stirring at room temperature, more tetraphenylborato complex (0.020 g, 0.028 mmol) was added. The final spectrum showed increased intensities of the bands assigned to $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_5\text{Me})$ and $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)]^+$, while the bands of the initial molybdenum(0) complex had completely disappeared.

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