APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 9, 335–340 (1995)

# On the Reactions of Molybdenum and Tungsten Carbonyls with Trimethyl- and Triethyl-aluminium

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**Reactions of hexacarbonylmolybdenum, hexacarbonyltungsten and arene complexes of tricarbonylmolybdenum and tricarbonyltungsten with trimethyl- and triethyl-aluminium have been studied. It has been found, based on IR and NMR spectra, that trialkylaluminium does not form complexes with hexacarbonyls of molybdenum and tungsten. Arene (mesitylene, toluene and benzene) complexes of tricarbonylmolybdenum form 1 : 1 complexes with triethylaluminium, and arene complexes of tricarbonyltungsten form complexes with trimethyl- and triethyl-aluminium. Regardless of the molar ratios of reactants (arene)$M(CO)_3/AlEt_3$, only one of the three CO groups bonded to molybdenum or tungsten forms a complex with $AlEt_3$.**

**Fast exchange between free and complexed trialkylaluminium and an exchange of trialkylaluminium between all three carbonyl groups have been observed in benzene, toluene and decalin solutions. In the $^1H$ NMR spectra of the products of the reactions of (mesitylene)$Mo(CO)_3$ with $AlEt_3$ and $AlMe_3$, signals at −9 to −14 ppm (characteristic for molybdenum hydrides) were present. It confirmed an alkylation of molybdenum followed by $\beta$- or $\alpha$-hydrogen elimination with the formation of the corresponding molybdenum hydrides, the actual catalyst of aromatic hydrocarbon hydrogenation.**

**Keywords: molybdenum; tungsten; aluminium; catalysis of aromatic hydrocarbon hydrogenation**

## INTRODUCTION

Catalytic hydrogenation of unsaturated hydrocarbons (also of aromatic ones) with the use of gaseous hydrogen has been known and applied on an industrial scale for many years. However, Ziegler-type homogeneous catalysts for these processes have been little studied. Preparation of this type of catalyst usually consists of the reaction of a transition-metal compound with an organometallic compound of the main group metal—most commonly with organoaluminium compounds $R_3Al$.

We have previously found that the systems $M(CO)_6 + Et_3Al$ ($M = Mo$, W) catalyse hydrogenation of aromatic hydrocarbons with gaseous hydrogen (180–220 °C, 50 atm).[1]

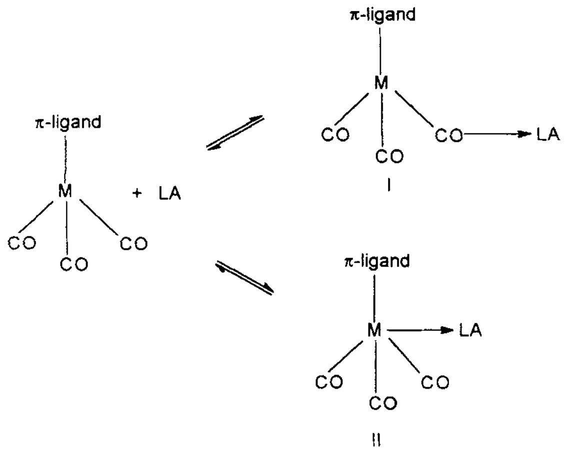
Transition-metal carbonyls in the presence of organoaluminium compounds reveal catalytic activity in many reactions. Vol'pin observed that the system $Re_2(CO)_{10} + Et_3Al$ or $(i\text{-}Bu)_2AlH$ catalysed hydrogenolysis of saturated hydrocarbons at 150–180 °C under a pressure of hydrogen of 100 atm.[2] We have shown that the systems $M(CO)_6 + M'(acac)_n + Et_3Al$ ($M = W$, Mo; $M' = Co$, Ni; $n = 2, 3$; acac = acetoacetate) catalyse hydrocracking of toluene and methylcyclohexane at 360–420 °C under 100 atm pressure of hydrogen[3] and $Mo(CO)_6$ catalyses cracking of aliphatic hydrocarbons.[4] It has also been revealed that systems composed of tungsten carbonyls and organoaluminium compounds catalyse olefin metathesis, e.g. $W(CO)_6 + AlX_3$; $W(L)(CO)_5 + AlX_3$ ($L =$ phosphine, $CH_3CN$); $W(arene)(CO)_3 + AlX_3$ ($X = Br$, Cl; $X_3 = EtCl_2$).[5–7]

Monometallic transition-metal carbonyls have very weak basicity; therefore they do not form adducts with Lewis acids. Polymetallic carbonyls form adducts with strong Lewis acids (aluminium and boron halides). In these adducts complexes are formed with bridging carbonyl groups (the basicity of the CO bridging groups is higher than the basicity of the terminal ones).[8, 9]

Lokshin has studied reactions of many carbonyl compounds of the type $(L)M(CO)_3$ ($M = Cr$, Mo, W, Re; $L =$ cyclopentadienyl, arene) with Lewis acids ($AlCl_3$, $TiCl_3$, $SnCl_4$).[10, 11] He has observed that, depending on the solvent used, two types of complexes were formed. Complex **I**, with the Lewis acid (LA) bonded to the carbonyl group, was formed in benzene, whereas in dichloro-

CCC 0268–2605/95/040335–06

*Received 20 April 1994*
*Accepted 12 September 1994*



Scheme 1

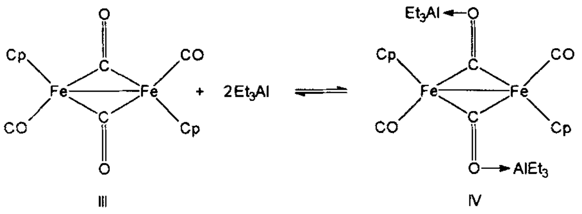
methane the Lewis acid was directly bonded to the metal atom (Scheme 1).

A complex of type **I**, formed initially in the reaction of $\eta$-$C_5H_5Re(CO)_3$ with $AlBr_3$, underwent rearrangement to complex **II** within 20 min.[12] The complexes formed were not isolated from the reaction mixture but were identified by means of IR spectroscopy. In the IR spectra of type **I** complexes, bands attributed to $\nu_{CO}$ were observed in two regions. Bands of free CO were shifted slightly towards higher frequencies in comparison with the spectra of the starting complexes. A strong, wide band, assigned to the complexed CO, appeared at 1700–1750 $cm^{-1}$. In IR spectra of type **II** complexes only bands assigned to the free CO groups were observed. They were shifted towards slightly higher frequencies that in the type **I** complexes.

Dimeric $[\eta$-$C_5H_5Fe(CO)_2]_2$ (**III**) reacts with 2 mol of $Et_3Al$ to form an adduct **IV**, where the aluminium atom is complexed only by bridging carbonyl groups (Scheme 2; Cp = $\eta$-$C_5H_5$).[13]

Adduct **IV** has been isolated in crystalline form and its structure has been confirmed by X-ray crystallography.

In the reactions of $[\eta$-$C_5H_5Fe(CO)_2]$ with $AlMe(BHT)_2$ [BHT = 2,6-di(t-butyl)-4-methylphenoxy], 1 : 1 and 1 : 2 adducts (depending on the molar ratio of the reactants) have been isolated.[14] In those adducts aluminium atoms are bonded to oxygen atoms of bridging carbonyl groups as in adduct **IV**.



Scheme 2

It can be assumed, based on literature data, that the first step of the reaction of transition-metal carbonyls with aluminium halides is the formation of complexes between the reactants. These complexes undergo further reactions to form transition-metal hydrides or alkyls and those compounds are the real catalysts of hydrogenation.

The purpose of this work was to find whether the complex between the organoaluminium compound and the transition-metal carbonyl was formed and whether one or more carbonyl groups took place in the complexation. The further goal of this work was to study the exchange reaction between free and complexed $R_3Al$ and the exchange of $R_3Al$ between various carbonyl groups.

## EXPERIMENTAL

All manipulations were carried out in an atmosphere of dry argon. $^{1}H$, $^{13}C$ and $^{27}Al$ NMR spectra were recorded on a Varian VXR 300 spectrometer. IR spectra were recorded on a Specord M80.

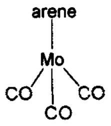
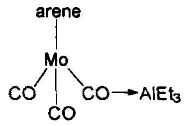
Triethyl- and trimethyl-aluminium ($Et_3Al$ and $Me_3Al$; Fluka AG) were distilled under reduced pressure prior to use.

Hexacarbonyl-molybdenum and -tungsten $Mo(CO)_6$ and $W(CO)_6$; [Merck] were purified by sublimation under reduced pressure. Aromatic hydrocarbons (benzene, toluene, mesitylene), hexane and heptane were dried and distilled over the benzophenone radical anion. Decalin was dried and distilled over potassium.

Arene complexes of molybdenum and tungsten were synthesized by the reactions of $Mo(CO)_6$ or $W(CO)_6$ with the arene according to methods described in the literature.[15]

A typical experiment was carried out as follows. (Arene)$M(CO)_3$ was placed in a Schlenk tube equipped with a magnetic stirring bar. A solvent (decalin, heptane, benzene-$d_6$ or toluene-$d_8$), in an amount giving a 1–5 wt % solution) was added at room temperature. A solution of trialkylaluminium was then added drop by drop, and the mixture was stirred at room tem-

**Table 1** Spectroscopic data of (arene)Mo(CO)$_3$ complexes[a]

| |  |  |
|---|---|---|
| Arene = benzene | | |
| IR (cm$^{-1}$) in heptane | $\nu_{(CO)}$ 1976, 1900 | $\nu_{(CO)}$ 1996, 1944<br>$\nu_{(CO \rightarrow Al)}$ 1750 |
| $^1$H NMR: $\delta$ (ppm) in $C_6D_6$ | 4.49 ($C_6H_6$) | 4.60 ($C_6H_6$)[b] |
| $^{13}$C NMR: $\delta$ (ppm) in $C_6D_6$ | 93.76 ($C_6H_6$)<br>221.05 (CO) | 97.7–98.1 ($C_6H_6$)[b]<br>223.67 (CO) |
| Arene = toluene | | |
| IR (cm$^{-1}$) in heptane | $\nu_{(CO)}$ 1984, 1912 | $\nu_{(CO)}$ 1996, 1940<br>$\nu_{(CO \rightarrow Al)}$ 1776 |
| Arene = mesitylene | | |
| IR (cm$^{-1}$) in decaline | $\nu_{(CO)}$ 1972, 1900 | $\nu_{(CO)}$ 1984, 1928<br>$\nu_{(CO \rightarrow Al)}$ 1768 |
| $^1$H NMR: $\delta$ (ppm) in $C_6D_6$ | 1.68 ($CH_3$), 4.35 (CH) | 1.57 ($CH_3$), 4.47 (CH)[b] |
| $^{13}$C NMR: $\delta$ (ppm) in $C_6D_6$ | 20.4 ($CH_3$), 93.2 (CH),<br>113.9 ($\underline{C}CH_3$), 223.3 (CO) | 20.4 ($CH_3$), 98.1 (CH),<br>119.1 ($\underline{C}CH_3$), 226.1 (CO)[b] |

[a] Reactions were carried out in heptane or decalin for IR spectra and in benzene-$d_6$ for NMR spectra.

[b] signals of $Et_3Al$ are omitted.

perature for 2 h. Such a prepared solution was then used for spectral measurements.

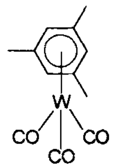
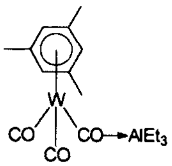
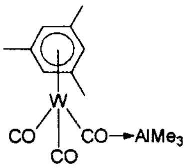
## RESULTS AND DISCUSSION

Reactions of $Mo(CO)_6$ and $W(CO)_6$ with $Me_3Al$ and $Et_3Al$ were studied. It was found, based on IR and NMR spectra, that organoaluminium compounds did not form complexes with the hexacarbonyls of molybdenum and tungsten.

Arene complexes of tricarbonylmolybdenum and tricarbonyltungsten react with $Et_3Al$ to form 1 : 1 complexes. Mesitylene (mes), toluene and benzene have been used as the arene. It was found that the complexes formed were catalysts for the hydrogenation of aromatic hydrocarbons.

IR, $^1$H and $^{13}$C NMR data for molybdenum complexes are presented in Table 1 and for tungsten complexes in Table 2. It appeared from the

**Table 2** Spectroscopic data of (mes)W(CO)$_3$ complexes[a]

| |  |  |  |
|---|---|---|---|
| IR (cm$^{-1}$) in decalin | $\nu_{(CO)}$ 1972, 1896 | $\nu_{(CO)}$ 1992, 1936<br>$\nu_{(CO \rightarrow Al)}$ *ca* 1750 | $\nu_{(CO)}$ 1992, 1932<br>$\nu_{(CO \rightarrow Al)}$ 1736 |
| $^1$H NMR: $\delta$ (ppm) in $C_6D_6$ | 1.81 ($CH_3$), 4.13 (CH) | 1.67 ($CH_3$), 4.22 (CH)[b] | 1.71 ($CH_3$), 4.24 (CH)<br>−0.31 ($CH_3$—Al) |
| $^{13}$C NMR: $\delta$ (ppm) in $C_6D_6$ | 19.9 ($CH_3$), 89.4 (CH),<br>109.2 ($\underline{C}CH_3$), 212.6 (CO) | 19.8 ($CH_3$), 94.4 (CH),<br>115.1 ($\underline{C}CH_3$), 216.1 (CO)[b] | 19.9 ($CH_3$), 93.4 (CH),<br>−7.2 ($CH_3$—Al), 215.5 (CO) |

[a] Reactions were carried out in decalin for IR spectra and in benzene-$d_6$ for NMR spectra.

[b] Signals of $Et_3Al$ are omitted.

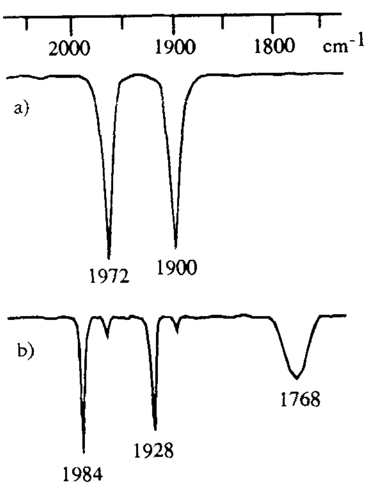


**Figure 1** IR spectra of (a) (mes)Mo(CO)$_3$; (b) post-reaction mixture of (mes)Mo(CO)$_3$ with E$_3$Al (1:3) in decalin.

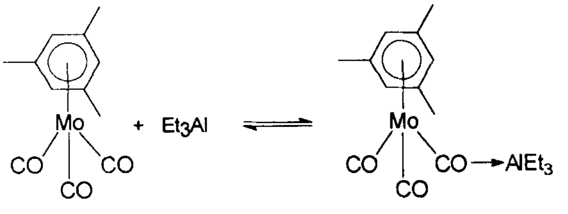
IR spectra that bands assigned to $\nu_{CO}$ were shifted 20–40 cm$^{-1}$ towards higher frequencies in comparison with the starting compounds and the bands assigned to $\nu_{CO \to Al}$ were shifted about 200 cm towards lower frequencies (Fig. 1). The above trends were true for all of the complexes studied.

In $^1$H NMR spectrum, the chemical shifts of CH$_3$ protons and CH protons of the mesitylene ring of the complex with Et$_3$Al differed from those in the starting compound by about 0.1 ppm. Also, the chemical shifts of carbon atoms in $^{13}$C NMR spectra changed in the complexes.

It appears from the above data that complexation proceeds via the carbonyl-group oxygen atom according to Scheme 3.

Regardless of the molar ratios of reactants (arene)M(CO)$_3$/Et$_3$Al, only one of the three CO groups bonded to molybdenum or tungsten forms a complex with Et$_3$Al. In the IR spectra of the complexes formed, besides the strongly shifted band of $\nu_{CO \to AlEt_3}$, only slightly shifted bands of $\nu_{CO}$ are also present.

Only single signals of protons and carbon atoms in the NMR spectra have been observed, due to fast exchange between free and complexes Et$_3$Al and also to exchange between various carbonyl groups (Fig. 2).



**Scheme 3**

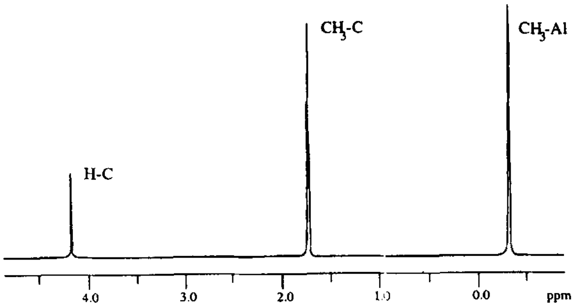


**Figure 2** $^1$H NMR spectrum of (mes)W(CO)$_3$ · AlMe$_3$ complex in benzene-d$_6$ at room temperature.

The $^{27}$Al NMR spectrum ($\delta = 161$ ppm) is characteristic for four-coordinate aluminium, which confirms a simple coordination of Et$_3$Al.

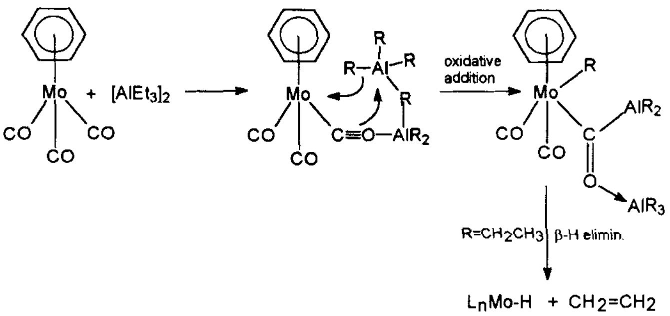
In contrast to Et$_3$Al, Me$_3$Al does not form a complex with (mes)Mo(CO)$_3$. IR, $^1$H and $^{13}$C NMR spectra remain unchanged after the addition of trimethylaluminium to the carbonyl compound. Due to the weak donor properties of the carbonyl group, bridging bonds in the dimer [Me$_3$Al]$_2$ (stronger than in [AlEt$_3$]$_2$) have not been cleaved.

Toluene and benzene complexes of tricarbonylmolybdenum, as for their mesitylene analogue, react with Et$_3$Al to form products where one carbonyl group is bonded to Et$_3$Al (Table 1).

(mes)W(CO)$_3$ formed complexes with Et$_3$Al and Me$_3$Al at a molar ratio of reactants of 1:1. Fast exchange between free and complexed trialkylaluminium and an exchange of trialkylaluminium between all three carbonyl groups were observed in benzene, toluene and decalin solutions. At room temperature, the chemical shifts of the protons of the methyl group bonded to aluminium depend on the molar ratio of the reactants (Table 3) and the chemical shifts of other signals remain unchanged.

**Table 3** $^1$H NMR spectra of (mes)W(CO)$_3$/Me$_3$Al in benzene-d$_6$

| Molar ratio (mes)W(CO)$_3$/Me$_3$Al | Chemical shift of CH$_3$—Al, $\delta$ (ppm) |
|---|---|
| 1/0.2 | −0.15 |
| 1/1.25 | −0.31 |
| 1/3 | −0.32 |
| 1/13 | −0.35 |
| 0/1 | −0.36 |



Scheme 4

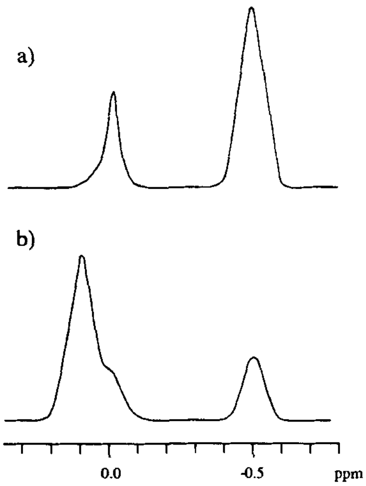
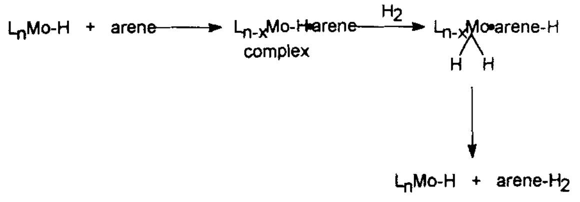


**Figure 3** Low-temperature $^1$H NMR spectra of (a) $Me_3Al$ (signals integration ratio 1:2); (b) post-reaction mixture of $Me_3Al$ with (mes)W$(CO)_3$ (1.25:1) (signals integration ratio 6:1). Temperature, −85 °C; solvent, toluene-$d_8$.

The higher the excess of $Me_3Al$ in the reaction mixture, the nearer is the chemical shift of $CH_3$—Al protons to the chemical shift of pure $Me_3Al$. This demonstrates a fast exchange of methyl groups between free and complexed $Me_3Al$.[16]

At −85 °C in toluene-$d_8$ solution, the exchange between free and complexed $Me_3Al$ is hindered. In the $^1$H NMR spectrum the signal of complexed $Me_3Al$ overlaps with the signal of the bridging $CH_3$ groups of the free $Me_3Al$ dimer (Fig. 3). Integration of the signal of the terminal methyl groups of free $Me_3Al$ allows us to calculate the ratio of complexed to free $Me_3Al$ (Fig. 3b). This calculation confirms the formation of a 1:1 complex, and the excess of $Me_3Al$ remains uncomplexed.



Scheme 5

In the $^1$H NMR spectra of the products of the reactions of (mes)Mo$(CO)_3$ with $AlEt_3$ carried out at large excess of $Et_3Al$ at room temperature and without solvent, new signals at $\delta$ −9 to −14 ppm of low intensity were present besides the signals mentioned above. These signals were characteristic for molybdenum hydrides.[17, 18] Similar signals were present in the spectra of products of the reactions of (mes)Mo$(CO)_3$ with $Me_3Al$. The above confirmed an alkylation of molybdenum followed by a $\beta$- or $\alpha$-hydrogen elimination with the formation of a corresponding molybdenum hydride.

A mechanism proposed for the formation of the molybdenum hydride is shown on Scheme 4. It is proposed that the reaction involved coordination of an $R_3Al$ dimer to the carbonyl-group lone pair followed by oxidative addition at molybdenum to generate an alkyl molybdenum. The next step involves $\beta$-hydrogen elimination from the ethyl ligand to generate the molybdenum ethylene hydride intermediate. The elimination of the ethylene moiety yields the molybdenum hydride complex. In case of a methyl group, instead of $\beta$-hydrogen elimination $\alpha$-hydrogenation elimination take place, also giving a molybdenum hydride complex.

The molybdenum or tungsten hydride formed, acts as a hydrogenation reagent towards complexed aromatic hydrocarbons. The catalyst in the form of a hydride is then recovered by oxidative addition of gaseous hydrogen. This closes a catalytic cycle for hydrogenation of aromatic hydrocarbons (Scheme 5).

A similar mechanism of hydrogenation of acenaphthylene with gaseous hydrogen in the presence of $Ru_3(CO)_{12}$ has been demonstrated by Nagashima *et al.*[19]

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