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ARENETRICARBONYL-MOLYBDENUM AND -TUNGSTEN COMPLEXES

A.N. NESMEYANOV, V.V. KRIVYKH, V.S. KAGANOVICH and M.I. RYBINSKAYA*
Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)

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Summary

A preparative method is described for the synthesis of arenetricarbonylmolybdenum complexes from tripyridinemolybdenum tricarbonyl and boron trifluoride etherate in the presence of arene. A series of compounds unavailable by the direct procedure [heating of $Mo(CO)_6$, with arene] was prepared. In case of 1,4-diphenylbutadiene and tolane these two methods were found to give different results. 1,4-Diphenylbutadiene and $Py_3Mo(CO)_3$ in the presence of $BF_3 \cdot O(C_2H_5)_2$ produce mono- and bi-nuclear arenemolybdenum tricarbonyl complexes, while $Mo(CO)_6$ affords bis(diphenylbutadiene)molybdenum dicarbonyl as the main product on heating. Unlike other arenes, tolane and $Py_3Mo(CO)_3$ yield tritolanemolybdenum carbonyl besides tolanemolybdenum tricarbonyl, whereas the direct procedure led to no arenetricarbonylmolybdenum complexes. The compounds obtained were identified by elemental analysis and IR.

Introduction

Several methods are known for the synthesis of the Group VI metal arenetricarbonyl derivatives. The direct method is the most common and simple: it involves heating metal hexacarbonyl in excess arene or with arene in a suitable solvent [1]. Some methods are based on the use of metal hexacarbonyl trisubstituted derivatives of the type $L_3M(CO)_3$, where L = CH_3CN [2], NH_3 [3], γ-picoline [4]. Other methods are only of minor significance.

The direct method was the most suitable for chromium compounds. This gave a great variety of arenetricarbonylchromium compounds, including those with different substituents in the benzene ring and in the side chain. In the case of molybdenum and tungsten, this method gave complexes generally with benzene and with some of its alkyl derivatives. This may be explained by high reaction temperature (100-200°C) resulting in decomposition of the generated complex or in by-processes. Arenetricarbonylmolybdenum derivatives are less stable than the respective tungsten and chromium complexes so their synthesis must be undertaken under milder conditions. We therefore employed the Öfele modified method [4] for the synthesis of arenemolybdenum tricarbonyl complexes, based on reaction of (γ-picoline)$_3$Cr(CO)$_3$ with arene in the presence of $BF_3 \cdot O(CH_3)_2$ under mild conditions.

Results and discussion

We found that the reaction of tripyridinemolybdenum tricarbonyl with boron trifluoride etherate in the presence of arene proceeds quickly and smoothly even at room temperature. Unlike the Öfele reaction it is not complicated by the formation of noticeable amounts of PyMo(CO)$_5$, and affords a high yield of arenemolybdenum tricarbonyl complexes (eqn. 1).

$$\mathrm{Py_3Mo(CO)_3 + arene + 3\ BF_3 \cdot O(C_2H_5)_2 \xrightarrow[20^\circ C]{ether} areneMo(CO)_3 + 3\ Py \cdot BF_3} \quad (1)$$

The reagents Py$_3$Mo(CO)$_3$, arene and $BF_3 \cdot O(C_2H_5)_2$ (in 1/1/3 mole ratio) were used. In the reaction with toluene it was shown that the yield of arenetricarbonyl complexes is weakly dependent on the arene excess. This fact is important in the use of scarce arenes.

We have thus prepared a series of previously unknown arenetricarbonylmolybdenum complexes. The melting points, yields, IR spectra and the data of elemental analysis are shown in Table 1. The yields of some arenemolybdenum tricarbonyl complexes prepared by us or by other authors employing the direct synthesis are also given for comparison. Thus the synthesis via the tripyridinemolybdenum tricarbonyl complex is more advantageous over the direct synthesis: it gives higher yields, shorter reaction time (1-2 h), the reaction may be carried out at room temperature with a minimum quantity of arene. Moreover, it should be noted that we failed to obtain compounds VII-X, XII, XIII, XVI, XVII, XX-XXIV by the direct method.

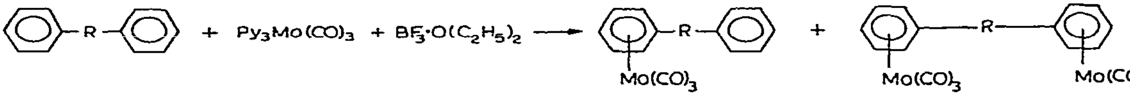
The arenetricarbonylmolybdenum compounds obtained are light-yellow crystalline substances soluble in organic solvents and decomposing rapidly in solution. Introduction of the alkyl substituents into the aromatic ring increases the stability of complexes. Thus three methyl groups produce such an increase in stability that one may obtain complexes with 1-acetyl- and 1-bromo-2,4,6-trimethylbenzene. The picture changes markedly in the absence of stabilizing alkyl groups: the reaction with acetophenone gives the mixture of acetophenonemolybdenum tricarbonyl complex, PyMo(CO)$_5$, and Mo(CO)$_6$ (identified by its IR spectrum in the metal carbonyl region). We failed to isolate acetophenonemolybdenum tricarbonyl due to its exceptional instability. Similar results were obtained in the case of bromobenzene.

We made an attempt to extend this method to the synthesis of arenetungsten tricarbonyl complexes. However, Py$_3$W(CO)$_3$ reacts with arene in the presence of $BF_3 \cdot O(C_2H_5)_2$ very slowly even upon refluxing in ether. In this case very low yield of arenetungsten tricarbonyl is obtained along with comparable amounts of PyW(CO)$_5$ and W(CO)$_6$. More drastic conditions (60°C, sealed ampoule) result in considerable decomposition with precipitation of metallic tungsten.

An attempt to use the molybdenum and tungsten complexes L$_3$M(CO)$_3$, where L$_3$ = (NH$_3$)$_3$ and $NH_2CH_2CH_2NHCH_2CH_2NH_2$ gave arenetricarbonyl complexes only in the case of (NH$_3$)$_3$Mo(CO)$_3$ but in low yield.

Thus the synthesis of arenetricarbonyl Group VIB metal derivatives from $Py_3M(CO)_3$ gives rather low yields with chromium, cannot be used for tungsten and is a preparative procedure for molybdenum complexes.

It was interesting to elucidate the behaviour of compounds containing an arene ring and unsaturated fragments in reaction 1. Potentially these compounds can coordinate with the metal carbonyl moiety in a variety of ways, thus giving a comparison with results of the direct synthesis. *trans*-Stilbene, 1,4-diphenylbutadiene and tolane were used as model compounds. Thus, mono- and bi-nuclear arenemolybdenum tricarbonyl complexes (eqn. 2) were obtained from tripyridinemolybdenum tricarbonyl and stilbene or 1,4-diphenylbutadiene in the presence of boron trifluoride etherate.



(2)

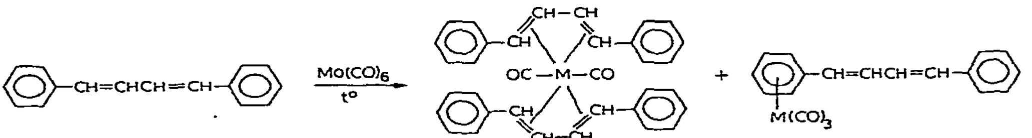
(XXI, R = CH=CH)

(XX, R = CH=CH; XXII, R = CH=CH—CH=CH)

(XXIII, R=CH=CH—CH=CH)

The 1/1 ratio of Ph—R—Ph to $Py_3Mo(CO)_3$ gives predominantly mononuclear derivatives and only the traces of binuclear compounds. The 1/2 ratio increases the yield of the binuclear complexes to 6%. They were also prepared from the equivalent quantities of mononuclear Ph—R—Ph · $Mo(CO)_3$, $Py_3Mo(CO)_3$ and $BF_3 \cdot O(C_2H_5)_2$. The binuclear compounds XXI and XXIII are red compounds, less soluble and more stable than the mononuclear complexes XX and XXII.

The direct reaction of stilbene with molybdenum and tungsten hexacarbonyls gave low yields of mononuclear complexes XX and XXVIII respectively. We failed to isolate pure XX from the reaction mixture and it was identified by its IR spectrum in the metal carbonyl region. The reaction of 1,4-diphenylbutadiene with molybdenum and tungsten hexacarbonyls led to bis(diphenylbutadiene)dicarbonyl complexes as the main products (eqn. 3) with the dienic fragment participating in coordination with the metal*. In these cases the mononuclear arenetricarbonyl complexes are produced in considerably lower yields. Analogously to the case with stilbene, the molybdenum complex was identified by its IR spectrum.



(3)

(XXII, M = Mo ; XXIX, M = W)

The direct reaction gives no binuclear arenetricarbonyl complexes. The structures of our first obtained bis(1,4-diphenylbutadiene)dicarbonyl-molybdenum and -tungsten complexes were established by comparison of IR metal

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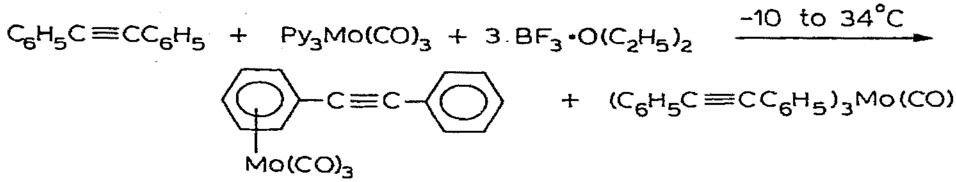
* It should be noted that the reaction of 1,4-diphenylbutadiene with $Cr(CO)_6$ results in coordination exclusively via the arenic fragment, giving mono- and bi-nuclear derivatives [9]. Thus in this reaction the behaviour of tungsten and molybdenum compounds differs essentially from that of chromium complexes.

carbonyl regions with those of other similar compounds described elsewhere [5-8].

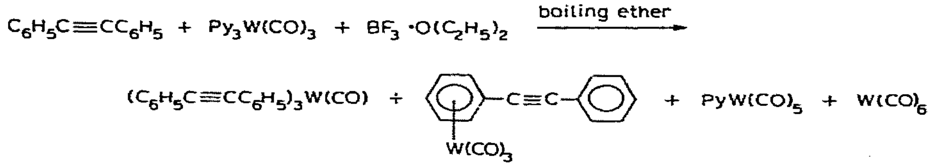
The course of the reaction of tolane with tripyridinemolybdenum tricarbonyl in the presence of boron trifluoride etherate is rather specific. Even at —10°C it affords 20% of tritolanemolybdenum carbonyl along with tolanemolybdenum tricarbonyl (eqn. 4).



(XXIV)

(4)

We failed to isolate the unstable arenetricarbonyl compound from the mixture and it was identified by its IR spectrum in the metal carbonyl region. The use of $Py_3W(CO)_3$ gives tritolanetungsten carbonyl as the main product (eqn. 5) (33%). The arenetricarbonyl compound is produced in negligible yield demonstrated by IR.



(5)

Thus the triple bond competes with the arene for the formation of bonding with molybdenum and tungsten.

It should be noted that the tritolanemonocarbonylmolybdenum complex has been obtained in 14% yield by refluxing $Mo(CO)_6$ with PhC≡CPh in the mixture of CH_3CN/C_6H_6 and by photochemical reaction in benzene using the same reagents (yield 20%) [10]. The respective tungsten complex was prepared from tolane and $(CH_3CN)_3W(CO)_3$ or $CH_3CNW(CO)_5$ [11,12] or by UV irradiation of the mixture of $W(CO)_6$ with tolane in benzene [10].

In the view of previously published data and our own results the reaction of molybdenum and tungsten carbonyls with tolane gave no arenetricarbonyl complexes. Thus $Mo(CO)_6$ or $W(CO)_6$ heated in a hydrocarbon yielded no arenetricarbonyl compounds even in trace amounts as demonstrated by IR. The molybdenum [13] and tungsten [14] carbonyls are known to react with tolane on heating affording a great variety of complexes and organic products. Thus the reaction of tolane with tripyridinetricarbonyl -molybdenum and -tungsten complexes may be recommended for the synthesis of tritolanemonocarbonyl complexes of these metals.

Hence the use of $Py_3Mo(CO)_3$ has enabled the list of known arenetricarbonylmolybdenum derivatives to be considerably expanded. It should be noted, however, that the ligands with a labile hydrogen atom or halogen (2-phenylethyl alcohol, phenylacetylene, benzyl chloride) produce only traces of arenemolybdenum tricarbonyl compounds detectable only by IR spectra. Generally the process involves considerable decomposition, giving rise to metallic molybdenum, molybdenum hexacarbonyl, pyridinemolybdenum pentacarbonyl, and unidentified products. Introduction of methyl groups into the arene ring caused no noticeable change in the results. It should be noted, however, that in the case of these arenes the negative results are not due to instabilities of the respective arenemolybdenum tricarbonyl compounds. We found, for example, that 4-mesitylbutanoltricarbonylmolybdenum is quite stable. The latter compound was obtained by reduction of molybdenum tricarbonyl ethyl mesitylbutyrate complex with $LiAlH_4$ in ether. This transformation is the first example of a reaction in the arene fragment of arenemolybdenum tricarbonyls.

The IR spectra were measured for all prepared compounds (Table 1). For arenemetal tricarbonyl compounds two absorption bands A_1 and E in the view of C_{3v} local symmetry of $M(CO)_3$ group are observed as stretching modes of the metal carbonyl fragments. However, the E band splits in the case of compounds XIV and XV, which could be due to removal of degeneracy at the lower symmetry of complexes.

Experimental

$Py_3Mo(CO)_3$ [15], $Py_3W(CO)_3$ [15], $(NH_3)_3Mo(CO)_3$ [16], $(NH_3)_3W(CO)_3$ [17], $(NH_2C_2H_4NHC_2H_4NH_2)Mo(CO)_3$ [18] and $(NH_2C_2H_4NHC_2H_4NH_2)W(CO)_3$ [18] were prepared using the procedures described. The syntheses and isolation of the compounds investigated were performed under argon in absolute solvents. The IR spectra were taken in solution of cyclohexane or chloroform using an IKS-14A spectrometer, and in KBr pellets on an UR-20 spectrometer.

The synthesis of arenetricarbonylmolybdenum compounds from $Py_3Mo(CO)_3$ and arene

4.5 mmol of $BF_3 \cdot O(C_2H_5)_2$ was added dropwise with stirring to 1.5 mmol of finely dispersed $Py_3Mo(CO)_3$ and 1.5 mmol of arene in 50 ml of ether. After 2 h stirring at room temperature the mixture was diluted with 100 ml of hexane. The ethereal hexane solution was washed with cold water (3 × 100 ml), dried over Na_2SO_4 and evaporated until starting crystallization. The solution was allowed to stand for several hours in the dry ice and the solvent was decanted. The crystals produced were washed with cold pentane and dried under vacuo. If necessary repeated crystallization from hexane was performed. The yields, constants and the data of elemental analysis are given in Table 1.

The synthesis of arenetricarbonylmolybdenum compounds by the direct method

A mixture of 5 mmol of $Mo(CO)_6$, 25 mmol of arene in 10 ml of heptane and 15 ml of decane was heated for 8 h at 135°C. The solvent was removed under vacuo at a bath temperature of 100-120°C. After cooling, the residue was treated with hot hexane, the solution was filtered, evaporated until crystallization started, and allowed to stand for several hours in dry ice. The yields of arenemolybdenum tricarbonyl compounds in terms of starting $Mo(CO)_6$ are shown in Table 1.

The synthesis of arenetungsten tricarbonyl compounds from $W(CO)_6$ and arene

(A) 5 mmol of $W(CO)_6$, 25 mmol of arene, 10 ml of heptane and 15 ml of decane were heated to 160°C for 18 h. The mixture was cooled, filtered and evaporated under vacuum at a bath temperature of 100-120°C. The residue was

(continued on p. 192)

TABLE 1

ARENETRICARBONYL-MOLYBDENUM AND -TUNGSTEN COMPLEXES

No.	Compound	M.p.(°C)	Yield direct reaction	(%) reaction 1
I	$C_6H_6Mo(CO)_3$ [d]	115-120		65
II	$C_6H_5CH_3Mo(CO)_3$ [d]	118-120 (with decomp.)		68
III	$1,3,5\text{-}(CH_3)_3C_6H_3Mo(CO)_3$ [d]	115-160 [c]		71
IV	tetraline$Mo(CO)_3$	121-123 (dec.)	26	65
V	$C_6H_5(CH_2)_3CH_3Mo(CO)_3$	39-40	18	
VI	$p\text{-}(t\text{-}C_4H_9)_2C_6H_4Mo(CO)_3$	124-125	33	
VII	$C_6H_5CH_2CH_2ClMo(CO)_3$	66.5-67.5 (dec.)		64
VIII	$C_6H_5CH_2CH_2CH_2BrMo(CO)_3$	65-67 (dec.)		58
IX	$2,4,6\text{-}(CH_3)_3C_6H_2CH_2CH_2BrMo(CO)_3$	108-110 (dec.)		70
X	$2,4,6\text{-}(CH_3)_3C_6H_2BrMo(CO)_3$	117-122 [c]		66
XI	$C_6H_5OCH_3Mo(CO)_3$ [e]	60-65 (dec.)	10.7	58
XII	$C_6H_5CH_2CH_2OCH_3Mo(CO)_3$	28-30		56
XIII	$C_6H_5CH_2CH_2C(=O)CH_3Mo(CO)_3$	84-86 (dec.)		60
XIV	$2,4,6\text{-}(CH_3)_3C_6H_2C(=O)CH_3Mo(CO)_3$	103-104 (dec.)	5.2	63
XV	$2,4,6\text{-}(CH_3)_3C_6H_2(CH_2)_3COOC_2H_5Mo\text{-}(CO)_3$	106-107 (dec.)		74
XVI	$2,4,6\text{-}(CH_3)_3C_6H_2(CH_2)_4OHMo(CO)_3$	92-93	50 [f]	
XVII	$C_6H_5CH=CH_2Mo(CO)_3$	80-82 (dec.)		61
XVIII	$C_6H_5CH_2CH_2CH=CH_2Mo(CO)_3$	41-43	4.3	58
XIX	$C_6H_5(CH_2)_3CH=CH_2Mo(CO)$	37-38		60
XX	$C_6H_5CH=CHC_6H_5Mo(CO)_3$	90-95		65
XXI	$C_6H_5CH=CHC_6H_5[Mo(CO)_3]_2$	155-160 [c]		5
XXII	$C_6H_5CH=CHCH=CHC_6H_5Mo(CO)_3$	127-132 [c]		60
XXIII	$C_6H_5CH=CHCH=CHC_6H_5[Mo(CO)_3]_2$	160-165 [c]		6
XXIV	$C_6H_5C\equiv CC_6H_5Mo(CO)_3$			
XXV	$C_6H_5CH_2CH_2CH=CH_2W(CO)_3$	13-15	2	1
XXVI	$C_6H_5(CH_2)_3CH=CH_2W(CO)_3$	17-18	3.5	
XXVII	$3,5\text{-}(CH_3)_2C_6H_3CH_2CH_2CH=CH_2\text{-}W(CO)_3$	92-94	20	
XXVIII	$C_6H_5CH=CHC_6H_5W(CO)_3$	119-120	4	
XXIX	$C_6H_5CH=CH\text{·}CH=CHC_6H_5W(CO)_3$	153-155 (dec.)	6	
XXX	$2,4,6\text{-}(CH_3)_3C_6H_2(CH_2)_3COOC_2H_5W(CO)_3$	127-128	24	

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[a] In cyclohexane. [b] In KBr pellets. [c] Dec. without melt. [d] See refs. 1 and 21. [e] See ref. 20. [f] Indirect method of synthesis. [g] In $CHCl_3$.

$\nu(C\equiv O)$[a] (cm^{-1})	$\nu(C=O)$[b] (cm^{-1})	Elemental analysis found (calcd.)(%)			
		C	H	M	X
1982.5, 1913					
1980, 1910					
1972, 1897					
1975, 1901		50.10	3.91	29.81	
		(50.01)	(3.88)	(30.73)	
1981, 1909		49.76	4.62	30.58	
		(49.69)	(4.49)	(30.54)	
1975, 1899		54.99	6.03	26.07	
		(55.14)	(5.99)	(25.91)	
1980, 1910		41.20	2.79	30.00	11.20
		(41.21)	(2.83)	(29.93)	(11.06)
1980, 1911		38.09	2.98	25.39	21.25
		(38.02)	(2.92)	(25.31)	(21.08)
1969, 1894.5		41.56	3.66	23.37	19.73
		(41.29)	(3.71)	(23.57)	(19.63)
1975, 1903		38.36	2.98	25.36	20.37
		(38.02)	(2.92)	(25.31)	(21.08)
1981, 1907					
1977, 1906		45.44	3.95	30.06	
		(45.58)	(3.82)	(30.35)	
1979, 1911	1715	47.47	3.61	29.11	
		(47.57)	(3.69)	(29.24)	
1975^{1907}_{1900}	1695	49.12	4.43	28.88	
		(49.13)	(4.12)	(28.04)	
1968^{1899}_{1893}	1726	52.42	5.50	23.16	
		(52.18)	(5.35)	(23.16)	
1966, 1892		52.68	5.44	25.72	
		(51.62)	(5.41)	(25.77)	
1981, 1924		46.29	2.87	33.12	
		(46.50)	(2.84)	(33.77)	
1980, 1911		49.94	3.92	30.92	
		(50.01)	(3.87)	(30.74)	
1980, 1911		51.63	4.33	29.47	
		(51.54)	(4.32)	(29.41)	
1981, 1913		56.13	3.31	26.44	
		(56.68)	(3.36)	(26.64)	
1971, 1899[g]		44.67	2.24	34.93	
		(44.46)	(2.24)	(35.52)	
1980, 1913		59.20	3.77	24.70	
		(59.08)	(3.65)	(24.84)	
1972, 1895[g]		46.22	2.86	33.95	
		(46.66)	(2.49)	(33.89)	
1978, 1909					
1978, 1905					
1978, 1905					
1970, 1897		41.92	3.61	42.99	
		(42.08)	(3.77)	(42.94)	
1978, 1908		45.43	2.75	41.26	
		(45.55)	(2.69)	(41.04)	
1978, 1908		48.27	2.84	38.47	
		(48.12)	(2.97)	(38.79)	
1966, 1892	1725	43.25	4.36	36.51	
		(43.05)	(4.42)	(36.61)	

chromatographed on TLC plates with acid alumina Woelm using heptane/benzene (3/1) as eluent. Table 1 shows the yields of XXVIII and XXIX in terms of reacted $W(CO)_6$.

(B) 1 g of $W(CO)_6$ and 2 ml of arene were refluxed in a mixture of 50 ml of diglyme and 10 ml of heptane for 6 h. The solvent was removed in vacuo, and the residue chromatographed on an alumina column. The product was precipitated from CH_2Cl_2 with heptane. The yields of XXV-XXVII and XXX are shown in Table 1.

The reaction of 4-phenyl-1-butene with $Py_3W(CO)_3$ and $BF_3 \cdot O(C_2H_5)_2$

A mixture of 0.8 g of finely dispersed $Py_3W(CO)_3$, 1 ml of phenylbutene and 0.7 ml of $BF_3 \cdot O(C_2H_5)_2$ in 50 ml of ether was heated for 2 h in a sealed ampoule at 60°C. The mixture was filtered, washed with water, dried over Na_2SO_4 and evaporated to dryness. The residue was chromatographed on alumina plates in a mixture of petroleum ether/benzene (1/1). 7 mg (1%) of XXV and 12 mg (3.1%) of $PyW(CO)_5$, m.p. 112-114°C (from hexane) (lit. [19] 114°C) were eluated.

The reaction of tris(ammonia)tricarbonylmolybdenum with toluene and $BF_3 \cdot O(C_2H_5)_2$

A mixture of 0.25 g of $(NH_3)_3Mo(CO)_3$, 0.4 ml of $C_6H_5CH_3$ and 0.82 ml of $BF_3 \cdot O(C_2H_5)_2$ in 50 ml of ether was stirred for 3 days at room temperature. The mixture was filtered, the solution washed with water, dried over Na_2SO_4 and evaporated. The residue was crystallized from petroleum ether. 0.026 g (5%) of toluenemolybdenum tricarbonyl was obtained, m.p. 117-120°C (dec.) (lit. [20] 139-140°C).

The reaction of 1,4-diphenylbutadiene with $Mo(CO)_6$

0.66 g (2.5 mmol) of $Mo(CO)_6$ and 2.6 g (12.5 mmol) of 1,4-diphenylbutadiene in a mixture of 17 ml of heptane and 33 ml of decane was refluxed for 18 h at bath temperature 130°C. The mixture was cooled, filtered and the filtrate evaporated to dryness. The residue was chromatographed on a column with anhydrous Al_2O_3 using petroleum ether/benzene (10/1). 0.1 g (7%) of the orange bis(diphenylbutadiene)molybdenum dicarbonyl was eluated. M.P. 129-34°C (dec.). IR: $\nu(C\equiv O)$ 1931, 1978 cm^{-1} (Found: C, 71.89; H, 4.89; Mo, 16.89. $C_{34}H_{28}O_2Mo$ calcd.: C, 72.33; H, 4.89; Mo, 17.00%.)

The reaction of 1,4-diphenylbutadiene with $W(CO)_6$

0.7 g (2 mmol) of $W(CO)_6$, 2 g (10 mmol) of 1,4-diphenylbutadiene in the mixture of 17 ml of heptane and 33 ml of decane was refluxed for 18 h at a bath temperature of 160°C. The mixture was cooled to room temperature, filtered, and the filtrate evaporated to dryness. The residue was chromatographed on the column with anhydrous alumina using petroleum ether/benzene (10/1). 0.2 g (15%) of the orange bis(diphenylbutadiene)tungsten dicarbonyl was eluated. M.p. 148-153°C (dec.). IR: $\nu(C\equiv O)$ 1935, 1983 cm^{-1}. (Found: C, 62.52; H, 4.46; W, 28.12. $C_{34}H_{28}O_2W$ calcd.: C, 62.58; H, 4.32; W, 28.19%.)

The reaction of tolane with $Py_3Mo(CO)_3$ and $BF_3 \cdot O(C_2H_5)_2$

1.25 ml (9 mmol) of $BF_3 \cdot O(C_2H_5)_2$ was added to 0.54 g (3 mmol) of tolane and 1.26 g (3 mmol) of $Py_3Mo(CO)_3$ in 50 ml of ether at —10°C. The mixture was stirred for 1 h at —10°C and 15 min at room temperature. The mixture was filtered, the filtrate evaporated and the residue chromatographed on alumina plates using petroleum ether/benzene (10/1). 0.4 g (20%) of the light-yellow tritolanemolybdenum carbonyl was isolated. M.p. 144-146°C (dec.) (lit. [10] 150°C). IR: $\nu(C{\equiv}O)$ 2062 cm^{-1}. (Found: C, 78.46; H, 4.50; Mo, 14.78. $C_{43}H_{30}OMo$ calcd.: C, 78.41; H, 4.59; Mo, 14.57%.)

The reaction of tolane with $Py_3W(CO)_3$ and $BF_3 \cdot O(C_2H_5)_2$

1.25 g (9 mmol) of $BF_3 \cdot O(C_2H_5)_2$ was added to 0.81 g (9 mmol) of tolane and 1.55 g (3 mmol) of $Py_3W(CO)_3$ in 50 ml of ether. The mixture was refluxed for 7 h and 0.95 g of $Py_3W(CO)_3$ was obtained. The filtrate was evaporated to dryness and the residue chromatographed on alumina plates using petroleum ether/benzene (10/1). 0.1 g of $W(CO)_6$ and 0.014 g (3%) of $PyW(CO)_5$ [m.p. 112-113°C (from hexane) (lit. [19] 116°C] and 0.3 g (33% per reacted $Py_3W(CO)_3$) of the light-yellow tritolanetungsten carbonyl, m.p. 175-176°C (dec.) (from benzene/ethanol) (lit. [11,12] 193°C) were obtained.

The synthesis of 1-mesitylbutane-4-ol-molybdenum tricarbonyl

A suspension of 0.06 g of $LiAlH_4$ in ether was added gradually to an ethereal solution of 0.2 g (0.48 mmol) of $2,4,6\text{-}(CH_3)_3C_6H_2(CH_2)_3COOC_2H_5 \cdot Mo(CO)_3$, cooled to —70°C. The mixture was heated to 0°C and 1 ml of C_2H_5OH was added. The solution was washed with water, dried over Na_2SO_4, the ether evaporated to dryness and the residue crystallized from hexane. Yield 0.09 g (50%) of XVI (Table 1).

References

1 B. Nicholls and M.C. Whiting, J. Chem. Soc., (1959) 551; E.O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J.P. Mortensen and W. Semmlinger, Chem. Ber., 91 (1958) 2767; G. Natta, R. Ercoli and F. Calderazzo, Chim. Ind. (Milan), 40 (1958) 287.
2 R.B. King and G.A. Fronzaglia, Inorg. Chem., 6 (1967) 1837.
3 M.D. Rausch, G.A. Moser, E.J. Zaiko and A.W. Lipman, Jr., J. Organometal. Chem., 23 (1970) 185.
4 K. Öfele, Chem. Ber., 99 (1966) 1732.
5 E.O. Fischer, H.P. Kögler and P. Kuzel, Chem. Ber., 93 (1960) 3006.
6 H.P. Fritz, H. Keller and E.O. Fischer, Naturwiss., 48 (1961) 518.
7 R.B. King, P.M. Treichel and F.G.A. Stone, J. Amer. Chem. Soc., 83 (1961) 3593.
8 R.P.M. Werner and S.A. Manastyrskyi, J. Inorg. Nucl. Chem., 21 (1961) 278.
9 M. Cais and M. Feldkimel, Tetrahedron Lett., (1961) 444; F.M. Chaudhari, G.R. Knox and P.L. Pauson, J. Chem. Soc. C, (1967) 2255;
T.A. Manuel, S.L. Stafford and F.G.A. Stone, J. Amer. Chem. Soc., 83 (1961) 3597.
10 W. Strohmeier and D. von Hobe, Z. Naturforsch. B, 19 (1964) 959.
11 D.P. Tate and J.M. Augl, J. Amer. Chem. Soc., 85 (1963) 2174.
12 D.P. Tate, J.M. Augl, W.M. Ritchey, B.L. Rose and J.G. Grasselli, J. Amer. Chem. Soc., 86 (1964) 3261.
13 W. Hübel and R. Merenyi, J. Organometal. Chem., 2 (1964) 213.
14 W. Hübel, in J. Wender and P. Pino (Eds.), Organic Syntheses via Metal Carbonyls, New York, London, Sydney, 1968, p. 296.
15 W. Hieber and F. Mühlbauer, Z. Anorg. Allg. Chem., 221 (1935) 337.
16 W. Hieber, K. Englert and K. Rieger, Z. Anorg. Allg. Chem., 300 (1959) 295.
17 W. Hieber, K. Englert and K. Rieger, Z. Anorg. Allg. Chem., 300 (1959) 304.
18 E.W. Abel, M.A. Bennett and G. Wilkinson, J. Chem. Soc., (1959) 2323.
19 C.S. Kraihanzel and F.A. Cotton, Inorg. Chem., 2 (1963) 533.
20 W. Strohmeier, Chem. Ber., 94 (1961) 3337.
21 A.N. Nesmeyanov, L.V. Rybin, V.S. Kaganovich, V.V. Krivykh and M.I. Rybinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1973) 2090.