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# SYNTHESIS OF A STABLE $\sigma$-PHENYLMOLYBDENUM DERIVATIVE

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## SUMMARY

$\sigma$-Phenyl complex $C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_6H_5$ (I) was prepared for the first time using three different methods. On the basis of spectral data a *trans* configuration was assigned to the new complexes (I), $C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_2H_5$ (III) and $C_5H_5Mo(CO)_2[P(C_6H_5)_3]COC_6H_5$ (V). Decarbonylation of (V) was found to occur retaining *trans* configuration. Reactions of (I) with iodine and mercuric chloride have been investigated.

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The method involving arylation of cyclopentadienylmetal carbonyl anions with onium salts has been used by the authors for preparation of $\sigma$-aryl complexes of iron[1] and tungsten[2].

$$C_5H_5M(CO)_n^-Na^+ + (C_6H_5)_2I^+BF_4^- \rightarrow C_5H_5M(CO)_nC_6H_5 + [C_5H_5M(CO)_n]_2$$

$$M = Fe,\ n = 2$$
$$M = W,\ n = 3$$

The analogous molybdenum compound was not obtained by this method since the action of $(C_6H_5)_2IBF_4$ on $C_5H_5Mo(CO)_3^-Na^+$ results in the migration of phenyl group into cyclopentadienyl ring[2]:

$$C_5H_5Mo(CO)_3^-Na^+ + (C_6H_5)_2I^+BF_4^- \rightarrow [C_5H_5Mo(CO)_3]_2 + \\ + [(C_6H_5C_5H_4)Mo(CO)_3]_2 + (C_6H_5C_5H_4)Mo(CO)_6MoC_5H_5$$

It can be assumed that the dimeric products appear as a result of the rearrangement of $C_5H_5Mo(CO)_3C_6H_5$ occurring in *statu nascendi*. In our study of ligand effects on stability of the carbon–transition metal $\sigma$-bond it was of interest to prepare a stable $\sigma$-phenylmolybdenum derivative of the type $C_5H_5Mo(CO)_5LC_6H_5$ where L is a ligand replacing the CO group and stabilizing the molecule. Triphenylphosphine was employed as such a ligand. Three possible methods of preparation of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_6H_5$ have been studied:

(*a*). arylation of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]Na$ with diphenyliodonium fluoroborate;
(*b*). interaction of $(C_6H_5)_2Hg$ with $C_5H_5Mo(CO)_5[P(C_6H_5)_3]I$;
(*c*). decarbonylation of the corresponding benzoyl derivative, $C_5H_5Mo(CO)_2[P(C_6H_5)_3]COC_6H_5$, which is obtained via the reaction of benzoyl chloride with $C_5H_5Mo(CO)_2[P(C_6H_5)_3]Na$.

## RESULTS

Diphenyliodonium fluoroborate reacts vigorously with $C_5H_5Mo(CO)_2$-$[P(C_6H_5)_3]Na$ even at −70° in tetrahydrofuran:

$$C_5H_5Mo(CO)_2[P(C_6H_5)_3]^-Na^+ + (C_6H_5)_2I^+BF_4^- \rightarrow \underset{(I)}{C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_6H_5}\ (6\%) + \underset{(II)}{\{C_5H_5Mo(CO)_2[P(C_6H_5)_3]\}_2}\ (50\%) + C_5H_5Mo(CO)_2[P(C_6H_5)_3]I\ (5\%)$$

The yield of the desired product I is rather low but it is sufficiently stable. The main reaction product has been $\{C_5H_5Mo(CO)_2[P(C_6H_5)_3]\}_2$ briefly described in an earlier publication[3]. Pour solubility of (II) prevents its spectral investigation in solution and impedes its purification. C=O stretching frequences (in KBr pellet) are in accordance with those described in literature. Structure of complex (II) and absence of a substitution into cyclopentadienyl ring were confirmed by its reduction with Na/Hg to the corresponding anion followed by conversion to ethyl derivative after treatment with ethyl bromide:

$$(II) \xrightarrow{Na/Hg} C_5H_5Mo(CO)_2[P(C_6H_5)_3]Na \xrightarrow{C_2H_5Br} C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_2H_5\ (III)$$

Compound (III) was identified by elemental analysis, IR and NMR spectra. Formation of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]I$, used as starting reagent in preparation of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]Na$ may be referred both to incomplete reduction with sodium amalgam and to side reactions between iodonium salts and metal carbonyl anions which always give negligible amounts of the corresponding iodides.

Reaction of $(C_6H_5)_2Hg$ with $C_5H_5Mo(CO)_2[P(C_6H_5)_3]I$ in boiling benzene also leads to (I):

$$C_5H_5Mo(CO)_2[P(C_6H_5)_3]I + (C_6H_5)_2Hg \rightarrow \underset{(I)}{C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_6H_5}\ (8\%) + \underset{(IV)}{C_5H_5Mo(CO)_2[P(C_6H_5)_3]HgI}\ (5\%)$$

Major by-product of this reaction is $C_5H_5Mo(CO)_2[P(C_6H_5)]HgI$ (IV) previously obtained by another method[4]. Yields of (I) and (IV) are given on the basis of reacted $C_5H_5Mo(CO)_2[P(C_6H_5)_3]I$ since approximately 55% of starting iodide did not enter the reaction. Among other reaction products $C_6H_5HgI$ and $C_6H_5$–$C_6H_5$ were also identified. The UV irradiation leads to a negligible amount of (IV) although starting iodide conversion is somewhat better than in the thermal reaction in benzene.

Possibility of preparation of phenyl complex (I) from the corresponding benzoyl derivative $C_5H_5Mo(CO)_2[P(C_6H_5)_3]COC_6H_5$ (V) has been investigated. Complex (V) may be readily obtained by reaction of $C_6H_5COCl$ with respective anion:

$$C_5H_5Mo(CO)_2[P(C_6H_5)_3]^-Na^+ + C_6H_5COCl \xrightarrow[20^\circ C]{THF}$$

$$\rightarrow C_5H_5Mo(CO)_2[P(C_6H_5)_3]COC_6H_5 \quad \text{(V)}$$

Under conditions of decarbonylation of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]COCH_3$ into $C_5H_5Mo(CO)_2[P(C_6H_5)_3]CH_3$[5], *i.e.* in refluxing tetrahydrofuran, compound (V) gives no phenyl derivative (I) but undergoes decomposition. Its decarbonylation was conducted under mild conditions employing $Rh[P(C_6H_5)_3]_3Cl$ as a decarbonylating agent.

Complexes (I), (III), and (V) obtained for the first time are yellow crystalline substances, stable in air when solids, but decomposing in solutions, especially in polar solvents. Their IR and NMR spectra are listed in Table 1.

TABLE 1

IR AND NMR DATA OF COMPOUNDS (I), (III) AND (V)

| Compounds | $\nu$(CO)[a] | $\delta(C_5H_5)$[b] | $\delta(C_6H_5)$[b] | $\delta(C_2H_5)$[b] |
|---|---|---|---|---|
| $C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_6H_5$<br>(I) | 1859vs<br>1935s | d 4.84<br>$J$ 1.33 Hz | m 7.29–7.49 | |
| $C_5H_5Mo(CO)_2[P(C_6H_5)_3]COC_6H_5$<br>(V) | 1860vs<br>1943s<br>1603w | d 5.09<br>$J$ 1.33 Hz | m 7.16–7.53 | |
| $C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_2H_5$<br>(III) | 1850vs<br>1935s | d 4.71<br>$J$ 1.44 Hz | m 7.27–7.53 | 1.47–1.69 |

[a] In $cm^{-1}$, solvent: $CHCl_3$. [b] In ppm, solvent: $CDCl_3$; d: doublet; m: multiplet.

It can be seen from Table 1 that all three compounds exhibit two terminal CO group stretching frequencies in the IR spectrum with the low-frequency peak being of higher intensity. In the region of 1500–1600 $cm^{-1}$ the ethyl complex (III) shows no vibrations while σ-Ph complex (I) has two bands corresponding to the in plane vibrations of phenyl ring σ-bonded to Mo. Benzoyl derivative (V) exhibits three bands in this region, two being close to those of complex (I) and probably referring to the aromatic ring vibrations (1573 and 1588 $cm^{-1}$). The third 1603 $cm^{-1}$ frequency might be assigned to the carbonyl group. This problem is now under study. In the NMR spectrum the cyclopentadienyl ring protons of all three compounds produce doublet with spin–spin coupling constant of 1.4 Hz resulting from the proton coupling at $^{31}P$ nucleus. Employing dependences observed for complexes of the type $C_5H_5Mo(CO)_2[P(C_6H_5)_3]X$[6] [where X is halogen or $Sn(C_6H_5)_3$ group] *trans*-configuration should be assigned to all three compounds. Spectral properties of the σ-phenyl complex (I) are independent of the method of its preparation and always correspond to *trans* isomer.

Of σ-phenyl molybdenum derivatives only $Mo(C_6H_5)_3 \cdot 2\ C_6H_5Li \cdot 3\ (C_2H_5)_2O$[7] and $(C_6H_5)_3Mo$[8] are described. $C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_6H_5$ is the first stable σ-phenyl molybdenum complex containing cyclopentadienyl and carbonyl ligands. Attention may be drawn to the high thermal stability of the complex having the m.p. 169°.

No migration of phenyl group into the cyclopentadienyl ring occurred on heating (I) in its solid state near the m.p. or refluxing in high boiling solvents or subjecting to UV-irradiation. Phenyl radical, however, is readily eliminated from molybdenum atom in reactions with $HgCl_2$ and iodine. (I) readily arylates sublimate in benzene even at 20°. Reaction with iodine should be conducted below 0° to avoid predominant formation of decomposition products:

$$C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_6H_5 \left\{ \begin{array}{l} \xrightarrow{I_2} C_5H_5Mo(CO)_2[P(C_6H_5)_3]I \\ \xrightarrow{HgCl_2} C_5H_5Mo(CO)_2[P(C_6H_5)_3]Cl \\ \qquad\qquad\qquad\qquad\qquad + C_6H_5HgCl \end{array} \right.$$

## DISCUSSION

The best procedure tested for preparation of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]$-$C_6H_5$ was that employing $(C_6H_5)_2IBF_4$ as arylating agent. Although the yield of the desired complex (I) was rather low, the method allows to obtain a considerable amount of dimeric product (II) which could be used for generating $C_5H_5Mo(CO)_2[P(C_6H_5)_3]Na$ ions.

It should be pointed out that it is extremely difficult to obtain (II) by any other procedure[3]. Our results confirm the scheme presented in ref. 2 for arylation of $C_5H_5Mo(CO)_3Na$ with diphenyl iodonium fluoroborate. In this case we arrive at the stable $\sigma$-phenyl derivative (I) undergoing no rearrangement.

The most significant shortcoming of the method employing $(C_6H_5)_2Hg$ is a low conversion of starting iodide. Negligible difference in the chromatographic $R_f$ factors for $C_5H_5Mo(CO)_2[P(C_6H_5)_3]I$ and $C_5H_5Mo(CO)_2[P(C_6H_5)_3]HgI$ considerably complicates separation of the reaction products. Formation of the latter complex is not surprising since mercury resulting from the decomposition of the organic mercury compounds[9] may often produce mercury insertion products during the synthetic procedure. No desirable effect from UV-irradiation can be obtained because of a restricted stability of $\sigma$-phenyl complex (I) under prolonged UV-irradiation.

Decarbonylation reaction occurs under mild conditions with the use of $ClRh[P(C_6H_5)_3]_3$ as decarbonylating agent although the yield of (I) is small. It is of interest to note that in the case of decarbonylation reaction both the starting $\sigma$-benzoyl derivative and the resulting $\sigma$-phenyl complex (I) are *trans* isomers.

Results of Alexander and Wojcicki[10] for complexes of the type $C_5H_5Fe(CO)_2$-COR have proved that at first the elimination of the terminal CO group occurs which further combines with Rh atom and then it is followed by a migration of R from acyl group to a vacant coordination site. In this case one should expect the formation of *cis* isomer from the *trans* one. Apparently, the formation of *trans* isomer in this case may be attributed either to a fast transformation of the primarily generated *cis* isomer (I) to the *trans* isomer due to the higher thermodynamic stability of the latter or to a different mechanism of decarbonylation reaction in this case.

## EXPERIMENTAL

IR spectra were recorded on Model UR-10 spectrophotometer. NMR spectra were measured on a Perkin–Elmer R-12 instrument with hexamethyldisiloxane as internal standard. All experiments were conducted in an atmosphere of dry argon. Analytical data and m.p.'s are given in Table 2.

TABLE 2

| Compounds | Analysis found (calcd.) (%) | | | M.p. (°C) | Colour |
|---|---|---|---|---|---|
| | C | H | P | | |
| $C_5H_5Mo(CO)_2[P(C_6H_5)_3]COC_6H_5$ | 65.22<br>(65.76) | 4.28<br>(4.31) | 5.15<br>(5.30) | 140 | Yellow |
| $C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_6H_5$ | 67.53<br>(66.91) | 4.75<br>(4.52) | | 169 | Yellow |
| $C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_2H_5$ | 63.36<br>(63.78) | 4.87<br>(4.96) | | 142–143 | Yellow |

*Reaction of $C_5H_5Mo(CO)_2[P(C_6H_5)_3Na$ with $(C_6H_5)_2IBF_4$*

$(C_6H_5)_2IBF_4$ (5.5 g) was added, in small portions to a stirred and cooled solution of 15 mmoles (−70°) of $C_5H_5Mo(CO)_2P[(C_6H_5)_3]^-Na^+$ in anhydrous THF[6]. The reaction was fast even at −70°. The reaction mixture was slowly allowed to come to room temperature and stirred for another hour. Major quantity of (II) precipitated. It was filtered off, washed with hot alcohol to remove unreacted $(C_6H_5)_2$-$IBF_4$ and finally washed with ether. A red-crimson product (2.13 g 50 %) was obtained. Additional quantity of (II) can be isolated from the filtrate by chromatography. The filtrate was evaporated *in vacuo* and separated by thin layer chromatography on alumina with benzene/heptane mixture (1/1) as eluent. The yellow band coming first is $C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_6H_5$, the next red-crimson band is (II), the last red band contains starting material $C_5H_5Mo(CO)_2[P(C_6H_5)_3]I$. The products were extracted with methylene chloride and solvent was evaporated *in vacuo*. 0.3 g of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_6H_5$ (6%) and 0.45 g of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]I$ were obtained. Both products might be reprecipitated from a heptane/methylene chloride mixture with evaporation of the latter solvent *in vacuo*.

*Reaction of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]I$ with $(C_6H_5)_2Hg$*

A solution of 1.35 g of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]I$ in 100 ml of benzene with $(C_6H_5)_2Hg$ (1.6 g) was refluxed for 12 h. After evaporation of the solvent *in vacuo* the residue was extracted with minimum amount of chloroform and subjected to thin layer chromatography on alumina. The colourless alumina zone that comes before the yellow one containing the final product (I) was extracted with methylene chloride and the mixture $(C_6H_5)_2$ with the remaining unreacted $(C_6H_5)_2Hg$ was obtained. This mixture was again chromatographed using light petroleum. Besides the yellow band of (I), two other hardly separable zones were collected: a yellow one, $C_5H_5Mo(CO)_2$-$[P(C_6H_5)_3]HgI$, and a red band of the starting iodide. After extraction with methylene chloride and its vacuum evaporation 0.05 g of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_6H_5$ (8% on reacted iodide), 0.045 g of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]HgI$ (5 %) and 0.7 g of $C_5H_5$-$Mo(CO)_2[P(C_6H_5)_3]I$ were isolated. Residue insoluble in minimum amount of $CHCl_3$ gave some $C_6H_5HgI$.

### *Synthesis of $C_5H_5Mo(CO)_2P(C_6H_5)_3COC_6H_5$*

2 ml of $C_6H_5COCl$ in 10 ml of anhydrous THF was added dropwise while stirring to a cooled (0°) solution of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]Na$ {from 9 g of $C_5H_5$-$Mo(CO)_2[P(C_6H_5)_3]I$}. Mixture was allowed to come to room temperature and stirred for 2 h. After evaporation of the solvent under reduced pressure and extraction with chloroform the solution was chromatographed in benzene/heptane (1/1). The yield was 2.9 g (33%). Yellow crystals obtained were recrystallized from chloroform/heptane mixture (1/2).

### *Decarbonylation of $C_5H_5Mo(CO)_2P(C_5H_5)_2COC_6H_5$*

2.09 g of $[P(C_6H_5)_3]_3RhCl$ in 30 ml of $CH_2Cl_2$ was added dropwise to 1.35 g of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]COC_6H_5$ in 55 ml of $CH_2Cl_2$. The mixture was stirred at 30° for 8 h. Precipitated solid $[P(C_6H_5)_3]_2Rh(CO)Cl$ was filtered off, 1 g (65%). The filtrate was evaporated *in vacuo*, the residue extracted with methylene chloride and chromatographed on alumina column. A yellow band was eluted with benzene/heptane (1/1). After evaporation of the solvent 0.13 g of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]$-$C_6H_5$ (yellow crystals) was obtained (10%).

### *Synthesis of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_2H_5$*

A suspension of 2 g of $\{C_5H_5Mo(CO)_2[P(C_6H_5)_3]\}_2$ in 100 ml of anhydrous THF was added to a five-fold excess of 0.8% sodium amalgam. After stirring for an hour the solution was filtered and mixed with 2 ml of $C_2H_5Br$. After stirring for another hour the solvent was evaporated under vacuum, the residue extracted with methylene chloride and chromatographed on alumina. Yellow band was eluted with light petroleum. The yield was 0.8 g (40%). Reprecipitation from heptane/methylene chloride mixture with evaporation of the latter *in vacuo* gave compound having m.p. 140°.

### *Reaction of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_6H_5$ with $HgCl_2$*

0.4 g of (I) in 20 ml of benzene was stirred with 0.21 g of $HgCl_2$ for 2 h. Solvent was evaporated *in vacuo* and the residue extracted firstly with a minimum quantity of chloroform, then with acetone. Chloroform extract was chromatographed on alumina. 0.30 g (81%) of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]Cl$ was obtained and identified through its IR spectrum and chromatographic $R_f$ factor 0.09 g (42%) of $C_6H_5HgCl$ was isolated from acetone extract, m.p. 249°, identified by chromatography with a reference sample.

### *Reaction of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_6H_5$ with iodine*

A stirred solution of 0.089 g of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]C_6H_5$ in 5 ml of methylene chloride was cooled to $-50°$ and the solution of 0.041 g of iodine in 10 ml of the same solvent was slowly added. The reaction was completed as the mixture was allowed to come to 0°. Vacuum evaporation of the solvent and chromatography on alumina gave 0.063 g of $C_5H_5Mo(CO)_2[P(C_6H_5)_3]I$ (70%), identified through $R_f$ factor and IR spectrum.

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