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SYNTHESIS OF BENZOYL DERIVATIVES OF Mo AND W CYCLOPENTADIENYL TRICARBONYLS

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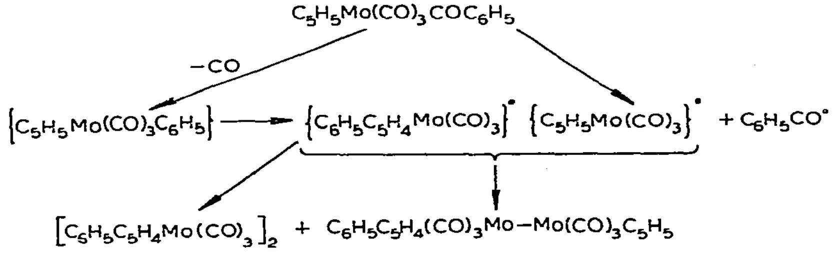
SUMMARY

Benzoyl compounds of the type $C_5H_5M(CO)_3COC_6H_5$ (M = Mo, W) have been synthesized. Decarbonylation of $C_5H_5Mo(CO)_3COC_6H_5$ proceeds readily and leads to the product $[C_6H_5C_5H_4Mo(CO)_3]_2$ in practically quantitative yield in which migration of the phenyl group to the C_5H_5 ring has occurred. The reaction of $C_5H_5M(CO)_3COC_6H_5$ with $P(C_6H_5)_3$ and $P(OC_6H_5)_3$ was found to proceed via two paths, *i.e.* replacement of a CO group and replacement of the C_5H_5 ring.

We have synthesized benzoyl derivatives of formula $C_5H_5M(CO)_3COC_6H_5$ (M = Mo, W) and investigated their ease of decarbonylation to the respective phenyl compounds. It is known that acyl compounds of the type $C_5H_5Mo(CO)_3COR$[1] are unstable in the case of Mo but of limited stability in the case of W. However, we have succeeded in preparing benzoyl compounds of Mo and W of similar type through the following reaction:

$$C_5H_5M(CO)_3^-Na^+ + C_6H_5COCl \rightarrow C_5H_5M(CO)_3COC_6H_5 \text{ (M = Mo, W)}$$

The compounds obtained have quite different stabilities. The W derivative is almost indefinitely stable in the solid state and only slowly decomposes in non-polar solvents, while the molybdenum compound is of limited stability in the solid state and rapidly decomposes in solutions at room temperature, even in non-polar solvents, according to the scheme:



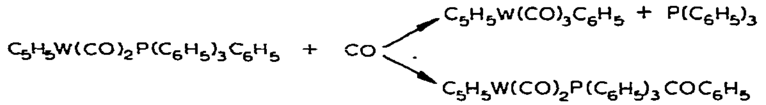
The same products were obtained during arylation of $C_5H_5Mo(CO)_3Na$ with $(C_6H_5)_2IBF_4$[2] but in this case the yield of $[C_6H_5C_5H_4Mo(CO)_3]_2$ (60%) was found to be much greater than that of $C_6H_5C_5H_4(CO)_3Mo{-}Mo(CO)_3C_5H_5$ (20%). If $C_5H_5Mo(CO)_3COC_6H_5$ is refluxed for 15 min in benzene then it is almost quantitatively converted to $[C_6H_5C_5H_4Mo(CO)_3]_2$ with some traces of $C_6H_5C_5H_4(CO)_3$-$Mo{-}Mo(CO)_3C_5H_5$ (by TLC). No diphenyl, benzophenone or dibenzoyl is apparently formed. The results obtained indicate that intramolecular transfer of the phenyl radical to the cyclopentadienyl ring occurs.

It is much more difficult to decarbonylate $C_5H_5W(CO)_3COC_6H_5$. Refluxing in benzene leaves the benzoyl compound virtually unchanged while refluxing in toluene results in the formation of traces of $C_5H_5W(CO)_3C_6H_5$ and almost complete decomposition of the starting material. The action of $ClRh[P(C_6H_5)_3]_3$ in benzene has little effect and leads to only a very small yield of $C_5H_5W(CO)_3C_6H_5$ although this decarbonylating agent is very effective in the case of $C_5H_5Mo(CO)_2P(C_6H_5)_3$-$COC_6H_4F$-*p*[3].

We have also studied the possibility of synthesizing benzoyl compounds of W cyclopentadienylcarbonyls by CO insertion in the $W{-}C_6H_5$ σ-bond of the respective phenyl derivatives. We have found that bubbling CO into a benzene solution of $C_5H_5W(CO)_3C_6H_5$ under UV irradiation affords $C_5H_5W(CO)_3COC_6H_5$ in 6% yield.

$$C_5H_5W(CO)_3C_6H_5 + CO \rightleftarrows C_5H_5W(CO)_3COC_6H_5$$

Apparently this reaction involves an equilibrium since increasing the reaction time results in virtually no increase in the yield of $C_5H_5W(CO)_3COC_6H_5$. With C_5H_5W-$(CO)_2P(C_6H_5)_3C_6H_5$[4] under the same conditions, in addition to CO insertion in the $W{-}C_6H_5$ σ-bond the reaction gives a product in which substitution of $P(C_6H_5)_3$ by carbon monoxide has occurred:



$$C_5H_5W(CO)_2P(C_6H_5)_3C_6H_5 + CO \begin{cases} \nearrow C_5H_5W(CO)_3C_6H_5 + P(C_6H_5)_3 \\ \searrow C_5H_5W(CO)_2P(C_6H_5)_3COC_6H_5 \end{cases}$$

The benzoyl compounds obtained exhibit different reactivities towards $P(C_6H_5)_3$ and $P(OC_6H_5)_3$. For example, $C_5H_5W(CO)_3COC_6H_5$ reacts with these ligands only after refluxing in benzene for many hours producing the substituted benzoyl compounds in almost quantitative yield. $C_5H_5W(CO)_3COC_6H_5 + L \rightarrow C_5H_5W(CO)_2LCOC_6H_5 + CO$ ($L = P(C_6H_5)_3$, $P(OC_6H_5)_3$). $C_5H_5Mo(CO)_3COC_6$-H_5, on the other hand, reacts with both $P(C_6H_5)_3$ and $P(OC_6H_5)_3$ either after standing in solution at room temperature for many hours or after refluxing in benzene for 1 h. In both cases two reactions occur: CO substitution by the L molecule and C_5H_5 ring substitution. The first reaction affords $C_5H_5Mo(CO)_2LCOC_6H_5$ but with $L = P(OC_6H_5)_3$ noticeable quantities of the decarbonylation product, C_5H_5Mo-$(CO)_2P(OC_6H_5)_3C_6H_5$ are also obtained. The second reaction yields a mixture of *cis-* and *trans-* $Mo(CO)_4L_2$ when $L = P(C_6H_5)_3$ and $Mo(CO)_3L_3$ in addition when $L = P(OC_6H_5)_3$.

$$C_5H_5Mo(CO)_3COC_6H_5 + P(C_6H_5)_3 \rightarrow \{[P(C_6H_5)_3]_3Mo(CO)_3\} \xrightarrow{CO} [P(C_6H_5)_3]_2Mo(CO)_4$$

$$C_5H_5Mo(CO)_3COC_6H_5 + P(OC_6H_5)_3 \rightarrow [P(OC_6H_5)_3]_3Mo(CO)_3$$

The compound $[P(C_6H_5)_3]_3Mo(CO)_3$ has already been isolated following

TABLE 1

REACTIONS OF $C_5H_5M(CO)_3COC_6H_5$ WITH $P(C_6H_5)_3$ AND $P(OC_6H_5)_3$(L) IN BENZENE

$C_5H_5M(CO)_3$-COC_6H_5	*L*	*Reflux time (h)*	*Yield (%)*			
			$C_5H_5M(CO)_2$-$LCOC_6H_5$	*$C_5H_5MCO_2LC_6H_5$*	*$L_3M(CO)_3$*	*cis, trans-$L_2M(CO)_4$*
M=Mo	$P(C_6H_5)_3$	1	36	traces		*trans* 6 *cis* 36
M=Mo	$P(OC_6H_5)_3$	2	33^a	20	8	*cis* traces
M=W	$P(C_6H_5)_3$	24	66	traces		*trans* traces
M=W	$P(OC_6H_5)_3$	40	45		2	

[a] Found: C, 60.40, 60.63; H, 4.14, 4.05; Mo, 15.00, 15.10; P, 4.84, 4.88. Calcd.: C, 60.77; H, 3.98; Mo, 15.17; P, 4.90%. ν(C≡O) 1895 vs, 1971 s cm^{-1}; ν(C=O) 1590 m cm^{-1} (solvent $CHCl_3$); PMR $\delta(C_5H_5)$ 4.87 (doublet) [$J(C_6H_5$–$P)$ 0.9 Hz], $\delta(C_5H_5)$ 7.18–7.62 (multiplet) ppm (solvent $CDCl_3$).

the rapid reaction of (cycloheptatriene)$Mo(CO)_3$ with $P(C_6H_5)_3$[5]. The instability of this complex in the conditions employed is apparently due to the fact that an approximately equivalent quantity of CO is evolved when CO substitution by L occurs thus enabling carbonylation of the intermediate tricarbonyl compound to occur. Thus the reaction of $C_5H_5Mo(CO)_3COC_6H_5$ with $P(C_6H_5)_3$ in boiling benzene is very similar to that of $C_5H_5W(CO)_3C_6H_5$ with $P(C_6H_5)_3$ under the same conditions[4].

When L=$P(OC_6H_5)_3$, substitution by CO is the principal reaction and only traces of *fac*-$Mo(CO)_3P(OC_6H_5)$ and *cis*-$Mo(CO)_4[P(OC_5H_5)_3]_2$ were obtained. These reactions are recorded in Table 1.

EXPERIMENTAL

PMR spectra were measured on a Perkin–Elmer R-12 instrument. All operations were carried out under argon.

1. *Synthesis of $C_5H_5Mo(CO)_3COC_6H_5$*

A solution of $C_5H_5Mo(CO)_3Na$ in 100 ml of absolute THF, obtained by reduction of 5.6 g of $C_5H_5Mo(CO)_3Cl$ with a double excess of 0.8% sodium amalgam, was slowly added under magnetic stirring to 1.6 ml of C_6H_5COCl in 10 ml of absolute THF cooled to −50°. The mixture was slowly heated to room temperature and the stirring continued for another half hour. The solvent was evaporated in vacuo, the residue was extracted with benzene/petroleum ether (2/8) and chromatographed on alumina. Elution with the same mixture gave 0.75 g of $[C_5H_5Mo(CO)_3]_2$ (15%), 0.15 g of $C_6H_5C_5H_4(CO)_3Mo$–$Mo(CO)_3C_5H_5$ (33%) and 0.5 g of $[C_5H_5Mo(CO)_3]_2Hg$ (7%). Elution with a mixture of petroleum ether and benzene (1/2) gave 1.25 g of $C_5H_5Mo(CO)_3COC_6H_5$ (18%). After low-temperature crystallization from hexane this material had m.p. 82–83°. (Found: C, 51.88; H, 2.98; Mo, 27.28. Calcd.: C, 51.45; H, 2.88; Mo, 27.40%.) ν(C≡O) 1934 vs, 2022 s cm^{-1}; ν(C=O) 1640 m cm^{-1} (solvent $CHCl_3$). PMR: $\delta(C_5H_5)$ 5.64 (singlet); $\delta(C_6H_5)$ 7.29–7.45 (multiplet) ppm (solvent $CDCl_3$).

2. *Synthesis of $C_5H_5W(CO)_3COC_6H_5$*

Using a similar procedure, 0.12 g of $[C_5H_5W(CO)_3]_2$ (4%) and 0.78 g of

$C_5H_5W(CO)_3COC_6H_5$ (18 %) were prepared from 3.68 g (0.01 mole) of $C_5H_5W(CO)_3$-Cl and 0.7 ml of C_6H_5COCl. After reprecipitation from a 1/1 hexane/CH_2Cl_2 mixture the material had a m.p. 143–144°. (Found: C, 41.07, 41.34; H, 2.29, 2.45; W, 41.72, 41.73. Calcd.: C, 41.12; H, 2.30; W, 41.97%.) $\nu(C{\equiv}O)$ 1935 vs, 2126 s cm^{-1}; $\nu(C{=}O)$ 1606 m cm^{-1} (solvent $CHCl_3$). PMR $\delta(C_5H_5)$ 5.67 (singlet); $\delta(C_6H_5)$ 7.29–7.45 (multiplet) ppm (solvent $CDCl_3$).

3. *Thermal decarbonylation of* $C_5H_5Mo(CO)_3COC_6H_5$

0.3 g of $C_5H_5Mo(CO)_3COC_5H_5$ in 30 ml of absolute benzene was refluxed for 20 min. Benzene was evaporated in vacuo. The residue was extracted with 5 ml of warm benzene. The insoluble residue was reprecipitated from heptane/methylene chloride while the latter was evaporated in vacuo. 0.16 g of $[C_6H_5C_5H_4Mo(CO)_3]_2$ was obtained. Chromatography of the benzene extract on alumina using a 2/8 mixture of benzene/heptane as eluant afforded 0.02 g of $C_6H_5C_5H_4(CO)_3Mo{-}Mo(CO)_3C_5H_5$ (8 %) and 0.03 g of $[C_6H_5C_5H_4Mo(CO)_3]_2$. Total yield of $[C_6H_5C_5H_4Mo(CO)_3]_2$ 71 %.

4. *Reactions of* $C_5H_5M(CO)_3COC_6H_5$ *with* $P(C_6H_5)_3$ *and* $P(OC_6H_5)_3$ *in boiling benzene*

The reflux times and product yields are shown in Table 1. In all experiments the ratio of $L/C_5H_5M(CO)_3COC_6H_5$ was 3/1. After evaporation of the benzene all the reaction mixtures were chromatographed on alumina using a mixture of petroleum ether and benzene (8/2). The order of elution was as follows: *trans*-$Mo(CO)_4L_2$, *cis*-$Mo(CO)_4L_2$, $C_5H_5M(CO)_2LC_6H_5$, $M(CO)_3L_3$ (only for $L{=}P(OC_6H_5)_3$) and $C_5H_5M(CO)_2LCOC_6H_5$. The complexes obtained were recrystallized from a 1/1 mixture of $CHCl_3{-}CH_3OH$ or reprecipitated from a mixture of heptane and methylene chloride by evaporation of the latter in vacuo.

5. *Reactions of* $C_5H_5W(CO)_3C_6H_5$ *and* $C_5H_5W(CO)_2P(C_6H_5)C_6H_5$ *with CO.*

6.6 g of $C_5H_5W(CO)_3C_6H_5$ in 150 ml of absolute benzene were irradiated with UV light (PRK-4) with CO bubbling for 40 h. After evaporation of the benzene in vacuo, the residue was dissolved in the mixture of benzene and hexane (1/1) and chromatographed on an alumina column using the same mixture as eluant. Two yellow bands were collected. The first band (5.5 g, 83 %) was identified as $C_5H_5W(CO)_3$-C_6H_5 and the second band (0.42 g, 6 %) as $C_5H_5W(CO)_3COC_6H_5$.

Similarly, 2.14 g of $C_5H_5W(CO)_2P(C_6H_5)_3C_6H_5$ in 150 ml of absolute benzene with bubbling of CO for 26 h and simultaneous UV irradiation gave 0.15 g of C_5H_5W-$(CO)_3C_6H_5$ (11 %), 1.5 g of $C_5H_5W(CO)_2P(C_6H_5)_3C_6H_5$ (70 %) and 0.14 g of $C_5H_5W(CO)_2P(C_6H_5)COC_6H_5$ (6.5 %).

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