The Photochemically-Induced Degradation of (η^5-C_5H_5)M(CO)_3 CH_3 Complexes (M = Cr, Mo, W)

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Photolysis, Degradation, Transition Metal Alkyls

The photolysis of (η^5-C_5H_5)M(CO)_3 CH_3 complexes (M = Cr, Mo, W) in solvents such as pentane, benzene or tetrahydrofuran results in cleavage of the methyl-metal sigma-bond and formation of the corresponding [(η^5-C_5H_5)M(CO)_3]_2 analogs as well as methane. Deuterium labeling studies indicate that, for the molybdenum system, abstraction of a hydrogen atom from a cyclopentadienyl ring by the methyl group represents a major reaction pathway for the production of methane. Photolysis of (η^5-C_5H_5)M(CO)_3 CH_3 complexes in CHCl_3 produces high yields of [(η^5-C_5H_5)CrCl]_2 in the case of the chromium analog, or (η^5-C_5H_5)M(CO)_3Cl where M = Mo or W.

Organometallic complexes of the type (η^5-C_5H_5)M(CO)_3 R represent excellent systems for detailed photochemical investigations, since not only are metal carbonyls known to be photolabile, but more recently the photolability of carbon-transition metal sigma-bonds and even (η^5-C_5H_5)M bonds have also been demonstrated. Previous photochemical studies on these systems have been largely concerned with reactions in the presence of donor ligands such as phosphines, phosphites, and acetylens, in which overall CO displacement is the predominate reaction pathway. We now report findings on the complexes (η^5-C_5H_5)M(CO)_3 CH_3 (M = Cr, Mo, W) which indicate that, in the absence of other donor ligands, photochemically-induced cleavage of the methyl-metal sigma-bond vis-à-vis the carbonyl-metal bond occurs.

One of us has previously reported that the photolysis of (η^5-C_5H_5)Cr(CO)_3 CH_3 in pentane solution results in the formation of two dimeric products, [(η^5-C_5H_5)Cr(CO)_3]_2 and [(η^5-C_5H_5)Cr(CO)_3]_2. Similar experiments involving (η^5-C_5H_5)Mo(CO)_3 CH_3 and (η^5-C_5H_5)W(CO)_3 CH_3 have now shown that the formation of [(η^5-C_5H_5)M(CO)_3]_2 complexes represents a general reaction pathway for the photodegradation of these Group VI-B metal alkyls (see Table). Analogous results were found in either pentane, benzene or tetrahydrofuran (THF) as the solvent. In general, longer photolysis periods produce slightly higher yields of the corresponding [(η^5-C_5H_5)M(CO)_3]_2 complexes, although in no case could conversions of > 40-50% be realized. Additional photo-degradative products which could not be separated or purified were invariably observed to be formed.

In contrast to the photolysis of (η^5-C_5H_5) Cr(CO)_3 CH_3, only trace amounts of the dimeric complex [(η^5-C_5H_5)Mo(CO)_3]_2 could be detected in the photolysis of (η^5-C_5H_5)Mo(CO)_3 CH_3 in pentane solution. We conclude that such dimeric M=M triple-bonded complexes are most likely secondary photoproducts derived from subsequent photodegradation of the initially produced [(η^5-C_5H_5) M(CO)_3]_2 species.

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Gas chromatographic analysis of the gas produced during the photolysis of the \((\eta^5-C_5H_5)M(CO)_3CH_3\) complexes showed it to be essentially pure methane in each case. In view of the well-known photolability of carbon monoxide in metal carbonyl complexes\(^1-3\), it was anticipated that CO would also be a major product in our studies. GLC analysis (thermal conductivity detector) of the gas produced during a 1.5 hour photolysis of \((\eta^5-C_5H_5)Mo(CO)_3CH_3\) in benzene solution, however, indicated that only methane was present (>3% CO could have been detected), and after a 6 hour photolysis, the ratio of CH\(_4\) to CO was still 6.5:1. Even more strikingly, photolysis of \((\eta^5-C_5H_5)Mo(CO)_3CH_3\) in the basic donor solvent THF for 1.5 hours afforded a gas whose analysis indicated a CH\(_4\) to CO ratio of 16:1. Clearly, photolytic cleavage of the metal-methyl bond and subsequent formation of methane predominates over M-CO cleavage in these photolyses.

In order to better understand the process by which methane is so readily produced in these reactions, the photolysis of several specifically deuterated systems was undertaken. Methane analysis was conducted by means of a mass spectrometric method using low ionizing voltages (ca. 20 eV) so as to minimize fragmentation. The photolysis of \((\eta^5-C_5H_5)Mo(CO)_3CD_3\) in C\(_6D_6\) afforded only CH\(_4\) and no deuterated methanes, indicating that in benzene at least, the solvent was not the source of the additional hydrogen atom. Photolysis of \((\eta^5-C_5H_5)Mo(CO)_3CD_3\) in C\(_6D_6\) produced CH\(_2\)D\(_2\) and CH\(_3\)D in a ratio of 2.8:1:1, indicating that hydrogen abstraction from the cyclopentadienyl ring by the departing methyl substituent represents a principal reaction pathway for the formation of methane.

\[
\begin{array}{c}
\text{CH}_3\text{D}_2 \\
\text{CD}_3
\end{array}
\]

Analogous findings have been observed in the photolysis of \((\eta^5-C_5H_5)Ti(CH_3)_2\) and deuterated analogs in hexane solution\(^21\). The formation of minor amounts of CH\(_2\)D\(_2\) and CH\(_3\)D indicates that some additional hydrogen-deuterium scrambling process must also be occurring during these photolyses. No CH\(_4\) or CD\(_4\) could be detected under these photolytic conditions, however, and the absence of the latter product indicates that intermolecular hydrogen abstraction from another methyl substituent is not a major reaction pathway leading to methane.

Photolysis of the \((\eta^5-C_5H_5)M(CO)_3CH_3\) complexes in chloroform proceeds in a somewhat different manner. Cleavage of the methyl-metal bond under methane formation is again observed in each case, however, the products are \([(\eta^5-C_5H_5)CrCl_2]_2\)\(^22\) in the chromium system, and \((\eta^5-C_5H_5)M(CO)_3Cl\) complexes in the case of the molybdenum and tungsten analogs. Formation of the \((\eta^5-C_5H_5)M(CO)_3Cl\) products during the photolysis of the corresponding \([(\eta^5-C_5H_5)M(CO)_3]_2\) complexes in CH\(_2\)Cl\(_2\) or CCl\(_4\) has

### Table. Photolysis of \((\eta^5-C_5H_5)M(CO)_3CH_3\) complexes in various solvents.

<table>
<thead>
<tr>
<th>M in ((\eta^5-C_5H_5)M(CO)_3CH_3)</th>
<th>Solvent</th>
<th>Time [h]</th>
<th>Yield [%]</th>
<th>([(\eta^5-C_5H_5)M(CO)_3]_2) (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>Pentane</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>Pentane</td>
<td>1.5</td>
<td>25(^b)</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>Pentane</td>
<td>6</td>
<td>31 (45)</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>Benzene</td>
<td>1.5</td>
<td>47 (50)</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>Benzene</td>
<td>6</td>
<td>25 (29)</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>THF</td>
<td>1.5</td>
<td>32 (32)</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>THF</td>
<td>6</td>
<td>45 (45)</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>Pentane</td>
<td>1.5</td>
<td>26 (28)</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>Pentane</td>
<td>6</td>
<td>12 (15)</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>Benzene</td>
<td>1.5</td>
<td>26 (28)</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>Benzene</td>
<td>6</td>
<td>25 (25)</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>THF</td>
<td>1.5</td>
<td>14 (14)</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>THF</td>
<td>6</td>
<td>14 (14)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Yields in parentheses are based on unrecovered starting material.

\(^b\) A 20% yield of \([(\eta^5-C_5H_5)Cr(CO)_3]_2\) was also obtained; see ref. 6.

\(^c\) Trace amounts of \([(\eta^5-C_5H_5)Mo(CO)_3]_2\) were also isolated in several runs.
previously been observed\textsuperscript{23–25}, as has the formation of \([\eta^5\text{C}_5\text{H}_5]\text{CrCl}_3\text{]}_2\) by the photolysis of either \([\eta^5\text{C}_5\text{H}_5]\text{Cr(CO)}_3\text{]}_2\), \([\eta^5\text{C}_5\text{H}_5]\text{Cr(CO)}_3\text{]}_2\) or \([\eta^5\text{C}_5\text{H}_5]\text{Cr(CO)}_3\text{]}_2\)NO in such solvents\textsuperscript{26}.

### Experimental Section

All solvents were dried and were freshly distilled under a nitrogen atmosphere. Mass spectral analyses were conducted on a Perkin-Elmer-Hitachi RMU-6L mass spectrometer.

**Photochemical preparation of \([\eta^5\text{C}_5\text{H}_5]\text{M(CO)}_3\text{]}_2\) complexes**

A 300-ml Schlenk tube containing a magnetic stirrer was attached to a mercury overpressure valve. The system was evacuated and flushed with purified nitrogen several times, and 1 mmole of the \([\eta^5\text{C}_5\text{H}_5]\text{M(CO)}_3\text{]}_2\) compound in ca. 250 ml of the appropriate solvent was added. The tube was then placed in a bath of ice water and photolyzed with a Hanovia (450 W) mercury high-pressure lamp for the specified time period (see Table). After photolysis, the solvent was removed under reduced pressure to a volume of ca. 5 ml, and added dropwise to 200 ml of pentane. The products precipitated immediately. The solution was decanted and the residue washed several times with 50-ml portions of pentane and dried under high vacuum. The yields of \([\eta^5\text{C}_5\text{H}_5]\text{CrCl}_3\text{]}_2\) and of \([\eta^5\text{C}_5\text{H}_5]\text{M(CO)}_3\text{]}_2\text{Cl}(\text{M} = \text{Mo, W})\) were nearly quantitative in all cases.

We are grateful to the National Science Foundation for financial support of this research program, to Profs. E. O. Fischer and M. HERRERHOLD for helpful discussions, and to the Deutscher Akademischer Austauschdienst (H. G. A.) and the Alexander von Humboldt-Stiftung (M. D. R.) for fellowships.

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