

The Photochemically-Induced Degradation of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{CH}_3$ Complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$)

M. D. RAUSCH and T. E. GISMONDI

Department of Chemistry, University of Massachusetts Amherst, Massachusetts, USA

H. G. ALT and J. A. SCHWÄRZLE

Anorganisch-chemisches Institut der Technischen Universität München

(Z. Naturforsch. **32b**, 998–1000 [1977]; received June 21, 1977)

Photolysis, Degradation, Transition Metal Alkyls

The photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{CH}_3$ complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) in solvents such as pentane, benzene or tetrahydrofuran results in cleavage of the methyl-metal sigma-bond and formation of the corresponding $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ 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 $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{CH}_3$ complexes in CHCl_3 produces high yields of $[(\eta^5\text{-C}_5\text{H}_5)\text{CrCl}_2]_2$ in the case of the chromium analog, or $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}$ where $\text{M} = \text{Mo}$ or W .

Organometallic complexes of the type $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{R}$ represent excellent systems for detailed photochemical investigations, since not only are metal carbonyls known to be photolabile^{1–3}, but more recently the photolability of carbon-transition metal sigma-bonds^{4–7} and even $(\eta^5\text{-C}_5\text{H}_5)\text{M}$ bonds^{7–9} 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 acetylenes, in which overall CO displacement is the predominate reaction pathway^{6, 10–14}. We now report findings on the complexes $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{CH}_3$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) which indicate that, in the *absence* of other donor ligands, photochemically-induced cleavage of the methyl-metal sigma-bond *vis-a-vis* the carbonyl-metal bond occurs*.

* The photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CH}_3$ in the presence of *trans*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$ produces a novel product derived from losses of both carbonyl and methyl substituents¹⁵, whereas photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CH}_2\text{C}_6\text{H}_5$ alone results in elimination of CO and formation of a novel π -benzyl derivative¹⁶.

Requests for reprints should be sent to Prof. M. D. RAUSCH, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003, USA.

One of us has previously reported that the photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{CH}_3$ in pentane solution results in the formation of two dimeric products, $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2]_2$.⁶ Similar experiments involving $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CH}_3$ and $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{CH}_3$ have now shown that the formation of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ complexes represents a general reaction pathway for the photo-degradation 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 produced slightly higher yields of the corresponding $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ 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 $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{CH}_3$, only trace amounts of the dimeric complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2]_2$ could be detected in the photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CH}_3$ in pentane solution. We conclude that such dimeric $\text{M}\equiv\text{M}$ triple-bonded complexes^{17–20} are most likely secondary photoproducts derived from subsequent photo-degradation¹⁷ of the initially produced $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ species.

Table. Photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{CH}_3$ complexes in various solvents.

M in $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{CH}_3$	Solvent	Time [h]	Yield [%] $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2^a$
Cr	Pentane	1.5	25 ^b
Mo	Pentane	1.5	31 (45)
Mo	Pentane	6	47 (50) ^c
Mo	Benzene	1.5	25 (29)
Mo	Benzene	6	47 (47)
Mo	THF	1.5	32 (32)
Mo	THF	6	45 (45)
W	Pentane	1.5	12 (15)
W	Pentane	6	26 (28)
W	Benzene	1.5	17 (17)
W	Benzene	6	25 (25)
W	THF	1.5	14 (14)
W	THF	6	14 (14)

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

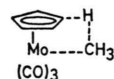
^b A 20% yield of $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2]_2$ was also obtained; see ref. 6.

^c Trace amounts of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2]_2$ were also isolated in several runs.

Gas chromatographic analysis of the gas produced during the photolysis of the $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{CH}_3$ complexes showed it to be essentially pure methane in each case. In view of the well-known photolability of carbon monoxide in metal carbonyl complexes¹⁻³, 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 $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CH}_3$ 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 $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CH}_3$ 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 $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CH}_3$ 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 $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CD}_3$ in C_6D_6 produced CHD_3 ,

CH_2D_2 and CH_3D 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.



Analogous findings have been observed in the photolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$ and deuterated analogs in hexane solution²¹. The formation of minor amounts of CH_2D_2 and CH_3D 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 $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{CH}_3$ 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 $[(\eta^5\text{-C}_5\text{H}_5)\text{CrCl}_2]_2$ ²² in the chromium system, and $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}$ complexes in the case of the molybdenum and tungsten analogs. Formation of the $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}$ products during the photolysis of the corresponding $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ complexes in CHCl_3 or CCl_4 has

previously been observed²³⁻²⁵, as has the formation of $[(\eta^5\text{-C}_5\text{H}_5)\text{CrCl}_2]_2$ by the photolysis of either $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$, $[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2]_2$ or $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_2\text{NO}$ in such solvents²⁶.

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 $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ complexes

A 300-ml Schlenk tube containing a magnetic stirrer was attached to a mercury overpressure valve. The system was evacuated and flushed with pre-purified nitrogen several times, and 1 mmole of the $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{CH}_3$ 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, the residue extracted with ethyl ether, and the extracts chromatographed on either Florisil or silica. Unreacted $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{CH}_3$ could be eluted with hexane, whereas elution with 1:1 hexane-benzene removed the $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ product. The dimeric complexes were identified by

PMR, IR and mass spectral comparisons with authentic samples.

Photolyses using deuterated materials were conducted in 25-ml Schlenk tubes equipped with a rubber septum and containing 10 mg of either $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CH}_3$ or $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CD}_3$ in 10 ml of C_6D_6 . The system was frozen at -78°C and pumped under high vacuum for 1 h before being allowed to thaw and irradiated as above.

Photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{CH}_3$ complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) in chloroform

In a typical run, 3 mmoles of the $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{CH}_3$ compound was dissolved in 300 ml of CHCl_3 . The yellow solution was irradiated under stirring for 1 h. In the case of the chromium reaction, a dark blue solution was produced, whereas in the molybdenum and tungsten systems, dark red solutions resulted. The reaction mixtures were then concentrated 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 $[(\eta^5\text{-C}_5\text{H}_5)\text{CrCl}_2]_2$ and of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}$ ($\text{M} = \text{Mo}, \text{W}$) 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. HERBERHOLD for helpful discussions, and to the Deutscher Akademischer Austauschdienst (H. G. A.) and the Alexander von Humboldt-Stiftung (M. D. R.) for fellowships.

- ¹ E. KOERNER VON GUSTORF and E. W. GREVELS, *Fortschr. Chem. Forsch.* **13**, 366 [1969].
- ² E. W. ABEL and F. G. A. STONE, *Quart. Rev. Chem. Soc.* **24**, 498 [1970].
- ³ M. WRIGHTON, *Chem. Rev.* **74**, 401 [1974].
- ⁴ H. ALT and M. D. RAUSCH, *J. Am. Chem. Soc.* **96**, 5936 [1974].
- ⁵ H. G. ALT and M. D. RAUSCH, *Z. Naturforsch.* **30b**, 813 [1975].
- ⁶ H. G. ALT, *J. Organometal. Chem.* **124**, 167 [1977].
- ⁷ R. W. HARRIGAN, G. S. HAMMOND, and H. B. GRAY, *J. Organomet. Chem.* **81**, 79 [1974].
- ⁸ E. VITZ and C. H. BRUBAKER, *J. Organomet. Chem.* **84**, C16 [1974].
- ⁹ E. VITZ, P. J. WAGNER, and C. H. BRUBAKER, *J. Organomet. Chem.* **107**, 301 [1976].
- ¹⁰ K. W. BARNETT and P. M. TREICHEL, *Inorg. Chem.* **6**, 294 [1967].
- ¹¹ A. N. NESMEYANOV, N. A. USTYNYUK, L. V. BOGATYREVA, and L. G. MAKAROVA, *Izv. Akad. Nauk S. S. R., Ser. Khim.* **1973**, 62.
- ¹² H. G. ALT, *Angew. Chem.* **23**, 800 [1976].
- ¹³ H. G. ALT and W. STADLER, *Z. Naturforsch.* **32b**, 144 [1977].
- ¹⁴ H. G. ALT, *J. Organomet. Chem.* **127**, 349 [1977].
- ¹⁵ R. B. KING and P. N. KAPOOR, *J. Organomet. Chem.* **18**, 357 [1969].
- ¹⁶ R. B. KING and A. FRONZAGLIA, *J. Am. Chem. Soc.* **88**, 709 [1966].
- ¹⁷ D. S. GINLEY and M. S. WRIGHTON, *J. Am. Chem. Soc.* **97**, 3533 [1975].
- ¹⁸ R. J. KLINGER, W. BUTLER, and M. D. CURTIS, *J. Am. Chem. Soc.* **97**, 3535 [1975].
- ¹⁹ J. POTENZA, P. GIORDANO, D. MASTROPAOLO, and A. EFRATEY, *Inorg. Chem.* **13**, 2540 [1974].
- ²⁰ P. HACKETT, P. S. O'NEIL, and A. R. MANNING, *J. Chem. Soc. Dalton Trans.* **1974**, 1625.
- ²¹ M. D. RAUSCH, W. H. BOON, and H. G. ALT, *J. Organomet. Chem.*, in press.
- ²² E. O. FISCHER, K. ULM, and P. KUZEL, *Z. Anorg. Allg. Chem.* **319**, 253 [1963].
- ²³ M. S. WRIGHTON and D. S. GINLEY, *J. Am. Chem. Soc.* **97**, 4246 [1975].
- ²⁴ C. GIANNOTTI and G. MERLE, *J. Organomet. Chem.* **105**, 97 [1976].
- ²⁵ R. M. LAINE and P. C. FORD, *Inorg. Chem.* **16**, 388 [1977].
- ²⁶ M. HERBERHOLD, R. KLEIN, and H. G. ALT, *Isr. J. Chem.*, in press.