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PHOTO-INDUCED DEGRADATION REACTIONS OF SOME ALKYL- AND ARYL-CARBONYL DERIVATIVES OF MANGANESE, MOLYBDENUM AND TUNGSTEN

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Summary

Photo-induced degradation of $CH_3Mn(CO)_5$ in pentane solution results in the formation of $Mn_2(CO)_{10}$, methane and carbon monoxide. Both CH_3D and CH_4 are formed when $CH_3Mn(CO)_5$ is photolyzed in C_6D_6. Photolysis of $C_6H_5CH_2Mn(CO)_5$ in pentane solution produces $Mn_2(CO)_{10}$, toluene and bibenzyl. Analogous photodegradation of $C_6H_5Mn(CO)_5$ in pentane solution yields $Mn_2(CO)_{10}$, benzene and carbon monoxide, but not biphenyl. The thermally unstable complex $C_2H_5Mn(CO)_5$ was studied by photolyzing it in solution at −40°C. GC analysis indicates that both ethylene and ethane are formed, and that the mole ratio of these products is dependent on the initial concentration of $C_2H_5Mn(CO)_5$. These results are consistent with a β-hydrogen elimination mechanism for this reaction. Photolysis of $CpMo(CO)_3CH_2C_6H_5$ in pentane solution produces $[CpMo(CO)_3]_2$ and toluene, whereas photolysis of $CpW(CO)_3CH_2C_6H_5$ affords $[CpW(CO)_3]_2$, $CpW(CO)_2(\eta^3$-benzyl), toluene, and a small amount (2%) of bibenzyl. When $CpM(CO)_2(\eta^3$-benzyl) (M = Mo, W) complexes are subjected to photolysis under similar conditions, the only identifiable product is toluene. $CpW(CO)_3C_6H_5$ degrades photochemically in pentane solution to form $[CpW(CO)_3]_2$ and benzene, together with a small amount (6%) of biphenyl.

Introduction

Since the initial reports that transition metal carbonyl alkyls can undergo photoinduced dealkylation in solution [1,2], research concerning the generality of these observations and the detailed mechanistic pathways by which they occur has been widespread. It now appears that the primary photoprocess for complexes of the type $CpM(CO)_nR$ (M = Cr, Mo, W, $n = 3$; M = Fe, $n = 2$; R = alkyl) is carbonyl dissociation to afford a 16-electron species, as proposed originally by Wojcicki for the photolysis of $CpW(CO)_3CH_3$ [3], and amply confirmed by the elegant matrix isolation studies of Rest and coworkers [4,5]. Photo-induced dealkylations of the complexes $CpM(CO)_3CH_3$ (M = Cr, Mo, W) and $CpFe(CO)_2CH_3$ in hydrocarbon solvents result in the formation of CH_4 via hydrogen abstraction [1–3,6] and radicals have been detected in some instances [7]. Complexes with alkyl ligands that contain β-hydrogen atoms (M = Mo or W, R = C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, etc.) also undergo photo-induced dealkylation in hydrocarbon solvents. However, in these cases the reactions have been shown to proceed via ejection of a CO ligand followed, in the absence of other ligands, by formation of olefin-hydrido complexes $CpM(CO)_2$(olefin)H [5,8–11].

In this paper, we report on photo-induced degradation reactions of a series of organomanganese carbonyls $RMn(CO)_5$ (R = CH_3, C_2H_5, $CH_2C_6H_5$, C_6H_5) as well as on similar reactions of $CpM(CO)_3CH_2C_6H_5$ (M = Mo, W) and $CpW(CO)_3C_6H_5$ in hydrocarbon solvents. These results have been previously discussed at a meeting [12].

Results and discussion

Studies on $RMn(CO)_5$ complexes (R = CH_3, C_2H_5, $CH_2C_6H_5$, and C_6H_5)

The photochemistry of methylpentacarbonylmanganese, $CH_3Mn(CO)_5$, offers both similarities and contrasts to the photochemical behavior of the $CpM(CO)_3CH_3$ compounds. Photochemical degradation of $CH_3Mn(CO)_5$ in pentane solution produced CH_4 and $Mn_2(CO)_{10}$, but the formation of these products proceeded more slowly than the formation of CH_4 and $[CpM(CO)_3]_2$ from the $CpM(CO)_3CH_3$ complexes of chromium, molybdenum and tungsten. The yield of $Mn_2(CO)_{10}$ was only 22% after 24 h of photolysis, and 6% of $CH_3Mn(CO)_5$ could be recovered, whereas virtually no starting material remained after photolyses of the $CpM(CO)_3CH_3$ complexes of similar concentration in pentane solution for 6 h [13].

Another major difference was illustrated by GC analysis of the gases formed from the photolysis of $CH_3Mn(CO)_5$ in pentane solution. There was more carbon monoxide found than methane, the CH_4/CO mole ratio being in the range of 0.35–0.58. This result is quite different from photolysis studies involving $CpW(CO)_3CH_3$, where the CH_4/CO ratio was typically around 1.50, and analogous studies of $CpMo(CO)_3CH_3$, where the CH_4/CO ratio ranged from 6.5/1 to greater than 30/1 [2,13]. It thus appears that loss of CO from $CH_3Mn(CO)_5$ under these photochemical conditions is much more facile than loss of CO from $CpM(CO)_3CH_3$ complexes, whereas loss of the methyl group from $CH_3Mn(CO)_5$ is less facile.

Studies designed to determine where the methyl group in $CH_3Mn(CO)_5$ acquires the additional hydrogen atom to form methane were considerably simpler than the corresponding determination for the $CpM(CO)_3CH_3$ complexes [2,13]. Photolysis of $CH_3Mn(CO)_5$ in C_6D_6 solution for 1 h produced methane, which upon mass spectral analysis at 20–25 eV indicated that the ratio of peaks at m/e 17 and 16 was 17/100, respectively. This result suggests that methane is formed by abstraction of hydrogen (or in this case, deuterium) from both another methyl group as well as from the solvent.

The photolysis of benzylpentacarbonylmanganese, $C_6H_5CH_2Mn(CO)_5$, also presents a contrast to the behavior of the $CpM(CO)_3CH_2C_6H_5$ complexes upon photolysis (see below). A 24 h photolysis of a 3.01 mM pentane solution of $C_6H_5CH_2Mn(CO)_5$ resulted in the formation of a 31% yield of toluene, a 22% yield of bibenzyl, and a 9% yield of $Mn_2(CO)_{10}$. No *trihapto*-benzyl product could be isolated or detected spectroscopically. It may be that the manganese complex is undergoing CO loss followed by simple homolytic cleavage of the benzyl–manganese σ-bond, leading to the relatively high conversion to bibenzyl. Such a conclusion would be in agreement with the findings of Lappert and coworkers, who were able to detect both benzyl radicals and $Mn(CO)_5$ radicals by ESR spectroscopy during the photolysis of $C_6H_5CH_2Mn(CO)_5$ in the presence of the spin-trap nitrosodurene [14].

Photolysis of a 2.15 m*M* solution of phenylpentacarbonylmanganese, $C_6H_5Mn(CO)_5$, in pentane solution for 6 h also produced the hydrogen abstraction product benzene (55%) and $Mn_2(CO)_{10}$ (8%). However, the coupling product, biphenyl, could not be detected. The starting material $C_6H_5Mn(CO)_5$ was recovered in 39% yield, so that the yields of benzene and $Mn_2(CO)_{10}$ based on unrecovered starting material were 90 and 13%, respectively. Photolysis of $C_6H_5Mn(CO)_5$ in benzene solution for a similar time period did afford biphenyl in 5% yield, however.

In contrast to photo-induced degradation studies on $CH_3Mn(CO)_5$, $C_6H_5CH_2Mn(CO)_5$, and $C_6H_5Mn(CO)_5$, all of which are relatively thermally stable compounds, similar studies on ethylpentacarbonylmanganese, $C_2H_5Mn(CO)_5$, were appreciably more difficult, due to the very limited thermal stability of this species in solution. $C_2H_5Mn(CO)_5$ was best prepared by the method of Green and Nagy [15]. We should point out that the procedure originally given by Hieber and Wagner [16] for the synthesis of $C_2H_5Mn(CO)_5$ actually results in the formation of propionylpentacarbonylmanganese, $C_2H_5COMn(CO)_5$ [17].

The fact that $C_2H_5Mn(CO)_5$ and not $C_2H_5COMn(CO)_5$ was obtained from Green's preparation [15] was confirmed by the following observations: The substance was a light yellow oil, extremely air-sensitive and thermally unstable. At $-20°C$, it froze to a solid mass as reported by Green. In contrast, we have synthesized propionylpentacarbonylmanganese and have found it to be an air- and thermally-stable solid, with a m.p. of 57–58°C without decomposition *. When $C_2H_5Mn(CO)_5$ degrades thermally, e.g., at room temperature, crystals of $C_2H_5COMn(CO)_5$ can be sublimed from the residue, as stated by Green. An IR spectrum of pure $C_2H_5Mn(CO)_5$ could not be obtained, as indicated by the presence of a relatively weak metal acyl carbonyl stretching frequency at 1645 cm^{-1}. However, the terminal carbonyl stretches at 2105, 2000, 1980 and 1940 cm^{-1} were so much more intense (especially the latter 3 absorptions, as is typical for a $Mn(CO)_5$ moiety), that one must conclude the major carbonyl containing material in the sample was not $C_2H_5COMn(CO)_5$.

Photolysis studies on $C_2H_5Mn(CO)_5$ in solution were conducted at $-40°C$, due to the thermal instability of this compound at higher temperatures. GC analysis of the gases formed during the photo-induced degradation of $C_2H_5Mn(CO)_5$ showed that both ethylene and ethane were produced in an approximate mole ratio of 2/1. Moreover, the mole ratio of C_2H_4/C_2H_6 increased slightly with decreasing concentration of the $C_2H_5Mn(CO)_5$. These results are analogous to similar trends reported earlier for the photo-induced degradation of $CpFe(CO)_2C_2H_5$ in pentane solution [18]. They are also consistent with a β-hydrogen elimination mechanism as proposed previously for $CpFe(CO)_2C_2H_5$ [18] and for $CpM(CO)_3R$ complexes that contain β-hydrogen atoms [5,8-11].

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* Hieber and Wagner describe their product from the reaction of $NaMn(CO)_5$ and C_2H_5I as colorless, long air-stable needles, with a m.p. of 58°C [16].

Another relevant study was the photolysis of $C_2H_5COMn(CO)_5$. Since this compound was a minor contaminant in samples of $C_2H_5Mn(CO)_5$, it was of interest to determine its photochemical behavior under similar conditions. A sample of $C_2H_5COMn(CO)_5$ was prepared by reacting propionyl chloride with sodium pentacarbonylmanganate [17]. Photolysis of a 0.100 *M* solution of $C_2H_5COMn(CO)_5$ in THF at $-40°C$ followed by GC analysis of the gases formed during the course of the reaction gave an C_2H_4/C_2H_6 ratio of 0.0246/1, that is, the major gaseous product was ethane. Ethane would be the product expected if a homolytic cleavage of the metal–acyl bond occurred. Such a homolysis would form the propionyl radical, which should spontaneously degrade to form CO and an ethyl radical. The latter could then abstract hydrogen, most likely from the solvent, to produce ethane. The ethylene formed from the photo-induced degradation of $C_2H_5COMn(CO)_5$ possibly results from $C_2H_5Mn(CO)_5$ formed by a CO extrusion reaction. This hypothesis was supported by photolyzing $C_2H_5COMn(CO)_5$ under 1 atm of CO. GC analysis of the gases formed demonstrated that ethane, but no ethylene, had been formed.

Studies on $CpM(CO)_3CH_2C_6H_5$ (M = Cr, Mo, W) and $CpW(CO)_3C_6H_5$

A second phase of this investigation has dealt with compounds of the type $CpM(CO)_3CH_2C_6H_5$ (M = Cr, Mo, W) and with $CpW(CO)_3C_6H_5$. Although $CpCr(CO)_3CH_2C_6H_5$ has been synthesized and characterized for the first time during the course of this program (see Experimental), we were not able to investigate its photoinduced degradation, due to the high thermal instability of this compound in solution above ca. $-20°C$ *. We did find, however, that thermal degradation of $CpW(CO)_3CH_2C_6H_5$ in pentane solution produced toluene, but not bibenzyl. Moreover, no evidence was found by IR spectroscopy for the formation of $CpCr(CO)_2(\eta^3$-benzyl).

The photochemical behavior of both *monohapto*- and *trihapto*-benzyl derivatives of molybdenum and tungsten was studied. The photochemical degradation of $CpMo(CO)_3CH_2C_6H_5$ has been reported by King and Fronzaglia to produce both $CpMo(CO)_2(\eta^3$-benzyl) as well as $[CpMo(CO)_3]_2$ [19]. However, these investigators employed very long photolysis periods and solutions that were much more concentrated than those normally used in our studies. Moreover, Cotton and Marks found that higher yields of $CpMo(CO)_2(\eta^3$-benzyl) could be formed by thermolysis rather than photolysis of $CpMo(CO)_3CH_2C_6H_5$ [20]. In any event, the photolysis of a 3.27 m*M* pentane solution of $CpMo(CO)_3CH_2C_6H_5$ for 6 h was found to produce a 33% isolated yield of $[CpMo(CO)_3]_2$, a 97% yield (by GC) of toluene, and no $CpMo(CO)_2(\eta^3$-benzyl) or bibenzyl.

A possible explanation for the failure to observe the formation of any *trihapto*-benzyl derivative was that the light intensity was effectively higher than in the more concentrated solution used by King, especially since any $[CpMo(CO)_3]_2$ formed in the reaction would act as an effective absorber of UV and visible light. Under our conditions, it is conceivable that any $CpMo(CO)_2(\eta^3$-benzyl) formed would subsequently undergo further photochemical degradation. In order to test this hypothesis, a sample of $CpMo(CO)_2(\eta^3$-benzyl) was prepared by thermal means [20], and then a

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* Equipment for conducting low-temperature photolyses was not available at the time this phase of the program was carried out.

0.50 m*M* solution of the compound in pentane was photolyzed for 6 h under conditions similar to the photolysis of $CpMo(CO)_3CH_2C_6H_5$. GC analysis indicated a quantitative yield of toluene, however, no other products including unreacted starting material could be isolated or identified. Thus, any *trihapto*-benzyl derivative formed under our photolysis conditions could undergo further photoinduced degradation.

The photochemical behavior of the analogous benzyl derivatives of tungsten offers some contrast to the behavior of the molybdenum analogs. Under conditions similar to those used for $CpMo(CO)_3CH_2C_6H_5$ (except that a 24 h rather than a 6 h photolysis period was used), $CpW(CO)_3CH_2C_6H_5$ produced a 10% yield of $[CpW(CO)_3]_2$ and a 34% yield of $CpW(CO)_2(\eta^3\text{-benzyl})$. Such a result indicates a far greater photolytic stability for $CpW(CO)_2(\eta^3\text{-benzyl})$ as compared to the molybdenum analog. The organic products from this reaction were toluene (21%) and bibenzyl (2%) *.

A solution of $CpW(CO)_3(\eta^3\text{-benzyl})$ in pentane (3.39 m*M*) was photolyzed for 6 h in order to determine if this compound was indeed more stable than $CpMo(CO)_2(\eta^3\text{-benzyl})$, and whether photolysis of the *trihapto*-benzyl compound would result in the same products as observed for the photolysis of $CpW(CO)_3CH_2C_6H_5$. Such an experiment could help establish whether the *trihapto*-benzyl compound is an intermediate in the reaction. The photolysis of $CpW(CO)_2(\eta^3\text{-benzyl})$ resulted in a 71% yield of toluene by GC analysis. Chromatography of the reaction products on alumina resulted in a 23% recovery of unreacted starting material. However, neither bibenzyl nor $[CpW(CO)_3]_2$ could be detected, and no other organometallic products could be isolated. These results suggest that two processes may be involved in the photochemically-induced degradation of the $CpM(CO)_3CH_2C_6H_5$ compounds. The first would be analogous to that of the $CpM(CO)_3CH_3$ analogs, and produces $[CpM(CO)_3]_2$ and toluene. The second process results in the formation of $CpM(CO)_2(\eta^3\text{-benzyl})$, which on further photolysis produces toluene and unidentified decomposition products.

Alt and coworkers [18] have previously examined the photo-induced degradation of $CpFe(CO)_2C_6H_5$. When this compound was photolyzed for 8 h in either pentane or hexane solution, the bimetallic complex $[CpFe(CO)_2]_2$ was formed in 79% yield (89% based on unreacted starting material). The major organic product was benzene (91%) accompanied by trace amounts ($< 1\%$) of biphenyl. In the present study, $CpW(CO)_3C_6H_5$ was photolyzed for 6 h in pentane solution, producing $[CpW(CO)_3]_2$ (29%), benzene (79%), and biphenyl (6%) **. No unreacted $CpW(CO)_3C_6H_5$ could be recovered. These results would seem to indicate a higher level of stability for the iron complex as compared to the tungsten derivative. When $CpFe(CO)_2C_6H_5$ was photolyzed in benzene solution, the yield of biphenyl increased from 1 to 26% [18]. Photolysis of $CpW(CO)_3C_6H_5$ in benzene solution likewise resulted in an increase in the yield of biphenyl from 6 to 16%.

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* The photo-induced conversion of $CpW(CO)_3CH_2C_6H_5$ to $CpW(CO)_2(\eta^3\text{-benzyl})$ has been independently observed by several other research groups, although yield data for the conversion and the nature of the organic products were not reported in detail [3,5,21].

** Since this program was completed [12,13], Alt and coworkers [5] have reported that photolysis of $CpW(CO)_3C_6H_5$ in pentane solution at −30°C for 1 h produces $[CpW(CO)_3]_2$ and C_6H_6 as the only products. No yield data was given.

Both of these results suggest the generation of phenyl radicals during the course of these reactions. However, it seems clear from other studies that the primary photochemical process occuring in these systems is the photo-ejection of a CO ligand to generate coordinately unsaturated species, which can then undergo further reactions. This conclusion is strongly reinforced by the matrix isolation studies of Rest and coworkers on $CpMo(CO)_3CH_3$ [4], $CpW(CO)_3CH_2C_6H_5$ and $CpW(CO)_3C_6H_5$ [5]. Matrix isolation studies on the analogous series of $RMn(CO)_5$ should provide valuable comparative information concerning the mechanism of photo-degradation of these systems. We hope to initiate such a program as part of future studies in this area.

Experimental

All operations were carried out under a nitrogen atmosphere by means of standard Schlenk techniques. The nitrogen was first deoxygenated by means of a heated BTS catalyst column, then dried with H_2SO_4 and P_2O_5. Pentane and hexane were dried over calcium hydride and freshly distilled under argon. Tetrahydrofuran (THF), ethyl ether and diglyme were predried with KOH, then sodium wire, and finally distilled under argon from sodium-benzophenone. Deuterated solvents were dried over activated Linde 5A molecular sieves and were deoxygenated by subjecting them to three freeze-pump-thaw cycles.

All photolyses were conducted using a 450-W Hanovia medium-pressure mercury vapor lamp. The lamp was placed in a water-cooled immersion well, and the sample to be photolyzed was then positioned approximately 2.5 cm from the well in a Pyrex Schlenk tube (pressure-type, water-jacketed-type, or standard-type for low temperature photolyses). The Schlenk tube was fitted with a magnetic stirrer and attached to an oil bubbler.

^1H NMR spectra were recorded on a Varian A-60 spectrometer, IR spectra on a Beckman IR-10 or Perkin–Elmer 237B spectrometer, and mass spectra on a Perkin–Elmer-Hitachi RMU-6L mass spectrometer. Melting points were determined in sealed tubes under nitrogen and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts.

Organic products were analyzed using a Varian Aerograph 2400 gas chromatograph equipped with a flame ionization detector and a Houston Instruments Omniscribe recorder. Gaseous compounds were separated on a $5' \times 1/8''$ Porapak Q column, using nitrogen at a flow rate of 15 ml/min as the carrier gas. For methane, ethane, ethylene and propane, the column was maintained at 50°C. For biphenyl and bibenzyl, the injector was set at 200°C and the column was programmed to increase from 50 to 150°C at a rate of 20°C/min. An Aerograph Autoprep gas chromatograph with a thermal conductivity detector was used to analyze for H_2 and CO, as well as to determine CO/CH_4 ratios. These gases were separated on a $10' \times 1/4''$ 13X molecular sieve column using helium at a flow rate of 60 ml/min as the carrier gas. Molar response ratios were determined by injecting known amounts of the compounds being studied and integrating. Peaks were identified both by retention time and by spiking. Yields of benzene, toluene, biphenyl and bibenzyl were calculated from their concentrations as determined by integrating their peaks relative to solutions of known concentrations of the compounds.

$Mo(CO)_6$ was generously donated by Climax Molybdenum Co., $Cr(CO)_6$ and $W(CO)_6$ were purchased from Pressure Chemical Co., and $Mn_2(CO)_{10}$ was obtained from Strem Chemicals. $C_2H_5Mn(CO)_5$ [15], $CpMo(CO)_3CH_2C_6H_5$ [19], $CpW(CO)_3CH_2C_6H_5$ [22], and $CpW(CO)_3C_6H_5$ [23] were prepared according to literature methods.

Preparation of sodium pentacarbonylmanganate

Sodium pentacarbonylmanganate was prepared by a modification of the method of King [24]. A 250-ml 3-neck round bottom flask was fitted with a gas inlet, a magnetic stirring bar, and a mercury overpressure valve. After evacuating the apparatus and flushing with nitrogen, mercury (45 ml, 585 g) was added. While stirring the mercury, sodium sand (5.85 g, 0.25 mol) was added slowly, resulting in an exothermic reaction. The dilute sodium amalgam thus formed was allowed to cool to room temperature and a solution of $Mn_2(CO)_{10}$ (10.0 g, 0.025 mol) in 125 ml of THF was added. The mixture was stirred vigorously until all the yellow color due to the $Mn_2(CO)_{10}$ was discharged. The solution initially turned from yellow to dark red and finally to a dark gray-green; this process typically took about 2 h. The stirring was then stopped and the finely divided mercury was allowed to settle as much as possible. The solution was decanted and filtered through a frit. The THF was then removed from the filtrate at reduced pressure and the residue was washed several times with pentane. After drying the resultant light green solid at reduced pressure, the $NaMn(CO)_5$ was ready for use.

Preparation of methylpentacarbonylmanganese

Methylpentacarbonylmanganese was prepared by a modification of a literature method [25]. $NaMn(CO)_5$ (2.83 g, 0.013 mol) was added to 150 ml of ethyl ether in a Schlenk tube equipped with a magnetic stirring bar, and stirred to make a slurry. The Schlenk tube was then placed in an ice bath and the slurry was allowed to cool to 0°C. Iodomethane (10.0 ml, 3.16 mmol) was added, and a white precipitate of sodium iodide soon formed. After stirring at 0°C for 2 h, the reaction mixture was allowed to warm to room temperature and the solution was stirred an additional 2 h to ensure complete reaction. The Schlenk tube was again placed in an ice bath and the solution was allowed to cool to 0°C. The solvent was removed very slowly at reduced pressure while the solution was maintained at 0°C in order to minimize loss of product due to volatilization. The resulting residue was extracted with pentane (150 ml), the extract was filtered through a frit, and the filtrate was allowed to cool to −78°C in a dry ice-acetone bath. The resultant light yellow crystals were collected by filtration and sublimed at 25°C/0.05 Torr onto a probe cooled by dry ice. The off white crystals were collected and resublimed to afford 2.93 g (54%) of $CH_3Mn(CO)_5$.

Preparation of benzylpentacarbonylmanganese

Benzylpentacarbonylmanganese was prepared by a modification of a literature method [25]. $NaMn(CO)_5$ (4.19 g, 0.0192 mol) was placed in a Schlenk tube which had been fitted with a magnetic stirring bar. Ethyl ether (150 ml) was added and the mixture was stirred to form a slurry. To this slurry was added benzyl chloride (2.0 ml, 2.2 g, 0.017 mol) and the resultant solution was stirred at room temperature for 12 h. The solution was now pale green and a white precipitate of sodium chloride had formed. This solution was filtered through a frit and the solvent was removed from the filtrate at reduced pressure. The resultant residue was extracted with pentane (5 × 50 ml) and the combined extracts were filtered through a frit. The filtrate was concentrated to ca. 50 ml at reduced pressure and allowed to cool to −78°C in an acetone-dry ice bath, resulting in the formation of crystals. The supernatant liquid was decanted and the crystals were washed with several ml of cold pentane. The crude product, which appeared to be contaminated with benzyl chloride, was dissolved in a minimum amount of pentane. The solution was chromatographed on a column of dry silica gel (Merck, Darmstadt, Silica for Column Chromatography, 100-200 mesh, with UV indicator) with pentane as the eluent, using a nylon column so that colorless bands could be visualized by means of UV light (an inert atmosphere was not provided for this step). The largest band was collected and the solvent was removed at reduced pressure. Recrystalliation of the residue from pentane gave 1.70 g (31%) of $C_6H_5CH_2Mn(CO)_5$ as white crystals, m.p. 36–37°C (lit. m.p. 37.5–38.5°C) [25].

Preparation of propionylpentacarbonylmanganese

A solution of $NaMn(CO)_5$ in THF was prepared by stirring 2.60 g (6.7 mmol) of $Mn_2(CO)_{10}$ in 100 ml of THF with a 10-fold excess of 1% sodium amalgam for 6 h. The solution was then decanted from the excess mercury and amalgam, and was filtered through a frit. The solvent was removed from the filtrate at reduced pressure, and 150 ml of ethyl ether was added to the residue. This mixture was stirred to form a slurry, and propionyl chloride (1.20 ml, 1.17 g, 13.0 mmol) was added dropwise. After stirring for 1 h, the solution was cooled to 0°C in an ice bath and the ethyl ether was slowly removed at reduced pressure. The residue was sublimed at 25°C under high vacuum onto a probe cooled by dry ice to give 0.056 g (17%) of $C_2H_5COMn(CO)_5$ as long white needles, m.p. 57–58°C (lit. m.p. 58°C) [16]. IR (pentane): ν(CO) 2020, 2000, 1960, 1645 cm^{-1}. ^{1}H NMR (C_6D_6): δ 2.35–2.70 (q, 2H, CH_2), 0.65–0.90 (t, 3H, CH_3).

Preparation of phenylpentacarbonylmanganese

A solution of lithium pentacarbonylmanganate [26] was produced by adding lithium triethylborohydride (12.5 ml of a 1 *M* solution in THF, 12.5 mmol) to a stirred solution of $Mn_2(CO)_{10}$ (1.95 g, 5.0 mmol) in THF (250 ml) which had been prepared in a Schlenk tube equipped with a rubber septum, an oil bubbler, and a magnetic stirring bar. The reactants were allowed to stir for 2 h at room temperature during which time gas was evolved and the color of the solution changed from yellow to red. Benzoyl chloride (1.20 ml, 1.45 g, 10.3 mmol) was added and the reaction mixture was stirred an additional 2 h at room temperature. The solvent was removed at reduced pressure, the residue was packed on silica (Merck, Darmstadt) and was chromatographed in air using a nylon column (see above). Elution with pentane brought down a yellow band of $Mn_2(CO)_{10}$ which was followed by a colorless band. The solvent was removed from the latter band and the residue was sublimed at 60°C/20 Torr to yield 0.76 g (28%) of $C_6H_5Mn(CO)_5$, m.p. 52.0–52.5°C (lit. m.p. 52°C [17]. IR (pentane): ν(CO) 2055, 2010, 2000, 1995 cm^{-1} (no absorbances between 1900 and 1580 cm^{-1}). ^{1}H NMR (CS_2): δ 6.85–7.85 (m, C_6H_5).

Preparation of benzyltricarbonyl(η^5-cyclopentadienyl)chromium

Cyclopentadiene (10 ml, 0.13 mol) was added to a slurry of sodium sand (2.30 g, 0.100 mol) in diglyme (125 ml) which had been prepared in a 250-ml 3-neck round bottom flask fitted with a gas inlet, a reflux condenser, an oil bubbler and a magnetic stirring bar. The mixture was stirred until gas evolution ceased. $Cr(CO)_6$ (18.0 g, 0.092 mol) was then added and the solution was refluxed for 2 h. The solvent was removed at reduced pressure and the resultant residue was dissolved in 125 ml of THF. The reaction mixture was then cooled to −20°C, benzyl chloride (11.5 ml, 0.10 mmol) was added, and the resultant mixture was stirred for 2 h at −20°C. The THF was removed at reduced pressure while the temperature was maintained at or below −20°C. The residue was extracted at −20°C with ethyl ether (5 × 50 ml) and the combined extracts were filtered through a frit. The filtrate was concentrated to ca. 100 ml under reduced pressure while maintaining the temperature at −20°C. The concentrated solution was then allowed to cool to −78°C in an acetone-dry ice bath, resulting in the formation of yellow crystals.. After 18 h, the supernatant solution was removed via a cannula. The crystals were dried at reduced pressure to produce 14.0 g (58%) of $CpCr(CO)_3CH_2C_6H_5$. Analytically pure samples were obtained by extracting the product with pentane at −20°C and filtering the extract directly into a Schlenk tube which had been precooled to −78°C. The pentane was decanted from the yellow powder which resulted and the procedure was repeated, after which the supernatant liquid was again decanted. This yellow powder was dried under high vacuum while allowing it to slowly warm from −78°C to room temperature over the course of several h. (Found: C, 61.58; H, 4.30; Cr, 17.4. $C_{15}H_{12}CrO_3$ calcd.: C, 61.65; H, 4.14; Cr, 17.7%). IR (Et_2O: ν(CO) 2005, 1935 cm^{-1}. ^1H NMR (acetone-d_6, −40°C): δ 6.60–7.30 (m, aromatic), 4.75 (s, C_5H_5), 2.75 (s, CH_2).

$CpCr(CO)_3CH_2C_6H_5$ is very air-sensitive and is thermally unstable, especially in solution. While it appears to be indefinitely stable at −20°C and for brief periods at room temperature in the solid state, it undergoes rapid decomposition at temperatures above −20°C in solution. This decomposition is accompanied by a color change from yellow to dark green, the formation of insoluble material, and the generation of toluene (but not bibenzyl) as determined by GC analysis of the supernatant liquid.

Photolysis of methylpentacarbonylmanganese in pentane solution

Methylpentacarbonylmanganese (1.00 g, 4.76 mmol) was placed in a 175-ml thick-walled pressure-type Schlenk tube which had previously been fitted with a magnetic stirring bar, evacuated, and flushed with nitrogen. Pentane (150 ml) was added and the mixture was stirred until all the $CH_3Mn(CO)_5$ had dissolved. The Schlenk tube was closed using an Ace-Threads polyethylene stopper and Viton O-ring as supplied by Ace Glass Co. The Schlenk tube and the immersion well were placed in an ice bath and the solution was photolyzed for 12 h. The solution, which was originally colorless and clear, became cloudy and yellow. The reaction mixture was concentrated to 50 ml at reduced pressure and chromatographed on a wet-packed column of alumina by elution with pentane. The colorless eluent yielded, after careful evaporation of the solvent at reduced pressure, 60 mg (6%) of the starting material $CH_3Mn(CO)_5$. A yellow band was next eluted. This fraction was concentrated to 50 ml at reduced pressure, and the concentrated solution was allowed to cool at −78°C. Yellow crystals which formed were separated, washed with cold pentane and dried at reduced pressure to yield 205 mg (22%) of $Mn_2(CO)_{10}$. No other metal-containing products could be isolated, identified or detected.

The relative amounts of methane and carbon monoxide formed during the photolysis of $CH_3Mn(CO)_5$ in pentane were determined as follows. A 4.80 mM solution of $CH_3Mn(CO)_5$ in pentane was prepared by dissolving 93.6 mg of $CH_3Mn(CO)_5$ in 100 ml of pentane. This solution was placed in a Schlenk tube fitted with a rubber septum and a magnetic stirring bar. The solution was then photolyzed and the gases evolved were sampled by syringe at various times and analyzed by GC. The CH_4/CO molar ratios were: 1.5 h, 0.434; 4.0 h, 0.574; 6.0 h, 0.356.

Photolysis of methylpentacarbonylmanganese in benzene-d_6

A 25-ml Schlenk tube was fitted with a rubber septum and the tube was evacuated and filled with nitrogen. $CH_3Mn(CO)_5$ (20 mg) and 10 ml of dried, degassed C_6D_6 was added. After the $CH_3Mn(CO)_5$ had dissolved, the solution was frozen, evacuated, and allowed to thaw. This cycle was repeated 3 times. The Schlenk tube was then placed in an ice bath and photolyzed for 1 h. The sample was removed from the bath and allowed to warm to room temperature. Benzene was added through the side arm, so that there was no longer a vacuum in the sample tube. This left a small headspace, consisting of gas evolved during the reaction, above the solution. Mass spectral analysis at 20 eV indicated the relative intensities of peaks at m/e 17 and 16 to be 17 and 100, respectively.

Photolysis of benzylpentacarbonylmanganese

A 3.01 mM solution of $C_6H_5CH_2Mn(CO)_5$ was prepared by dissolving 172 mg (0.60 mmol) of the compound in 200 ml of pentane. The solution was contained in a water-jacketed Schlenk tube equipped with a nitrogen inlet, a mercury overpressure valve and a magnetic stirring bar. After the solution was degassed, it was photolyzed for 14 h. GC analysis of the reaction mixture indicated that the yield of toluene was 31%. Work-up by column chromatography gave bibenzyl (14 mg, 22%) and $Mn_2(CO)_{10}$ (10 mg, 9%) as the only products which could be isolated.

Photolysis of phenylpentacarbonylmanganese

A 2.15 mM solution of phenylpentacarbonylmanganese, prepared by dissolving 117 mg of $C_6H_5Mn(CO)_5$ in 200 ml of pentane, was photolyzed in a water-jacketed Schlenk tube for 6 h, as described above. GC analysis indicated that CO was formed as the only gaseous product, and that the solution contained benzene in 55% yield. The solvent was removed from the reaction mixture at reduced pressure. Column chromatography of the residue on a dry-packed silica column using pentane as the eluent gave $Mn_2(CO)_{10}$ (7 mg, 8%) and unreacted $C_6H_5Mn(CO)_5$ (46 mg, 39%). No biphenyl could be detected by GC.

A similar photolysis of 138 mg of $C_6H_5Mn(CO)_5$ in 200 ml of benzene afforded 3 mg (5%) of biphenyl after chromatography.

Photolysis of ethylpentacarbonylmanganese

A 0.200 M solution of ethylpentacarbonylmanganese was prepared by dissolving 3.64 g of $C_2H_5Mn(CO)_5$ in 92.0 ml of THF at −40°C. Three other samples, 0.100, 0.058, and 0.034 M, respectively, were prepared by further diluting the 0.200 M sample. Each sample was photolyzed for 1 h at −40°C in Schlenk tubes that had been fitted with rubber septa. GC analyses of the gases produced during the photolyses were carried out by withdrawing gas samples via a syringe through the rubber septa. The C_2H_4/C_2H_6 molar ratios as a function of concentration were: 1.93, 0.200 *M*; 2.38, 0.100 *M*; 2.42, 0.058 *M*; 2.43, 0.034 *M*. Each result is the average of at least 10 injections, and the relative molar response factors for C_2H_4 and C_2H_6 were experimentally determined under identical GC conditions as used for the experimental samples.

Photolysis of propionylpentacarbonylmanganese

For the purpose of comparison, a 0.100 *M* solution of propionylpentacarbonylmanganese was prepared by dissolving 550 mg of $C_2H_5COMn(CO)_5$ in 20 ml of THF. The solution was then photolyzed for 1 h at −40°C as described for $C_2H_5Mn(CO)_5$. GC analysis of the gases produced indicated the C_2H_4/C_2H_6 ratio to be 0.246 as compared to 2.38 for 0.100 *M* $C_2H_5Mn(CO)_5$.

Photolysis of a similar solution under approximately 1 atm of CO pressure resulted in the exclusive formation of ethane.

Photolysis of benzyltricarbonyl(η^5-cyclopentadienyl)molybdenum

A solution of 192 mg of $CpMo(CO)_3CH_2C_6H_5$ in 175 ml of pentane (3.27 m*M*) was photolyzed for 6 h in a water-jacketed Schlenk tube, in the same manner as for the photolysis of $C_6H_5CH_2Mn(CO)_5$. The original orange-yellow solution yielded a turbid pale orange solution and a red-violet precipitate of $[CpMo(CO)_3]_2$ (52 mg, 33%). GC analysis of the solution showed that a 97% yield of toluene had been obtained, and that no detectable amounts of bibenzyl had been formed. Work-up of the supernatant solution by column chromatography yielded no starting material and no $CpMo(CO)_2(\eta^3$-benzyl).

Photolysis of benzyltricarbonyl(η^5-cyclopentadienyl)tungsten

Benzyltricarbonyl(η^5-cyclopentadienyl)tungsten (483 mg, 1.14 mmol) was placed in a water-jacketed Schlenk tube, dissolved in 2000 ml of pentane, and irradiated for 24 h. GC analysis of the solution showed that a 21% yield of toluene and a 2% yield of biphenyl had been obtained. The photolysis mixture was filtered, the solvent was evaporated, and the residue was chromatographed on a dry-packed silica column. Elution with 2/1 hexane/benzene brought down an orange band. The solvent was removed at reduced pressure and the residue was sublimed at 80°C/0.05 Torr to yield 154 mg (34%) of $CpW(CO)_3(\eta^3$-benzyl) as orange crystals. IR (Et_2O): ν(CO) 1960, 1870 cm^{-1} [3,5]. A 10% yield of $[CpW(CO)_3]_2$ was also obtained by column chromatography using 1/1 hexane/benzene as the eluent.

Photolysis of (η^3-benzyl)(η^5-cyclopentadienyl)dicarbonylmolybdenum

A solution of 30 mg of $CpMo(CO)_2(\eta^3$-benzyl) in 200 ml of pentane (0.50 *M*) was photolyzed for 6 h in a water-jacketed Schlenk tube. GC analysis indicated a 100% yield of toluene; no bibenzyl was detected. The solvent was evaporated and the residue was chromatographed on a dry-packed column of alumina. No organometallic products could be isolated.

Photolysis of (η^3-benzyl)(η^5-cyclopentadienyl)dicarbonyltungsten

A solution of 268 mg of $CpW(CO)_2(\eta^3$-benzyl) in 200 ml of pentane (3.39 m*M*) was photolyzed for 6 h in a water-jacketed Schlenk tube. GC analysis indicated a 71% yield of toluene. The solvent was evaporated and the residue was chromatographed on a dry-packed column of alumina. The column was eluted first with hexane and then with 3/1 hexane/benzene. GC analysis of the colorless forerun showed that no bibenzyl had been formed. The orange band which eluted in 3/1 hexane/benzene was found to be unreacted starting material, which was recovered in 23% yield. The yield of toluene was therefore 93% based on unrecovered starting material. No other organometallic compounds could be isolated.

Photolysis of phenyltricarbonyl(η^5-cyclopentadienyl)tungsten in pentane solution

A solution of 245 mg of $CpW(CO)_3C_6H_5$ in 200 ml of pentane (2.99 mM) was photolyzed for 6 h in a water-jacketed Schlenk tube as described previously. GC analysis of the resultant solution indicated that the yield of benzene was 79% and the yield of biphenyl was 6%. The solvent was removed at room temperature and the residue was chromatographed on a dry-packed silica column. Elution with 2/1 hexane/benzene gave a colorless forerun which contained biphenyl, and a red band which yielded 58 mg (29%) of $[CpW(CO)_3]_2$. No other products were detected.

Photolysis of phenyltricarbonyl(η^5-cyclopentadienyl)tungsten in benzene solution

A solution of 271 mg of $CpW(CO)_3C_6H_5$ in 200 ml of benzene (3.30 mM) was photolyzed for 6 h. Work-up by column chromatography as described above produced 52 mg (25%) of $[CpW(CO)_3]_2$. Unfortunately, the colorless forerun was lost due to an accident. Therefore, another solution was prepared by dissolving 258 mg of $CpW(CO)_3C_6H_5$ in 200 ml of benzene (3.15 M). After the solution was photolyzed for 6 h in a water-jacketed Schlenk tube, it was worked up by column chromatography on silica, eluting with 4/1 hexane/benzene up to the point where the red band of $[CpW(CO)_3]_2$ would have begun to elute. The solvent was evaporated to dryness and the residue was recrystallized from pentane to yield 7.8 mg (16%) of biphenyl as identified by GC.

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