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PHOTOCHEMICALLY INDUCED REACTIONS OF DECACARBONYLDIMANGANESE(0)

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Summary

Photolysis at ca. 350 nm of $Mn_2(CO)_{10}$ in the presence of each of I_2, CH_3I, SnI_4, $CuCl_2 \cdot 2\,H_2O$, HgX_2 (X = Cl, Br or I), C_6H_5HgI, η^5-$C_5H_5Cr(NO)_2Cl$, $(\eta^5$-$C_5H_5)_2Cr_2(NO)_4$ and $[Co_2(CNCH_3)_{10}](BF_4)_4$, generally under N_2 or CO in several organic solvents (mainly cyclohexane and THF), was investigated. The observed photoreactions are best rationalized in terms of initial homolytic cleavage of the Mn—Mn bond. In the presence of a halogen (X)-containing compound, the resultant $Mn(CO)_5^{\cdot}$ radical abstracts X to yield $Mn(CO)_5X$. These reactions are characterized by high quantum efficiencies (generally, $\phi_{-Mn_2(CO)_{10}} \gtrsim 0.36$). Following the abstraction, the remaining metal-containing species (usually a radical), $SnCl_3^{\cdot}$, CuCl, $HgX^{\cdot}$, $C_6H_5Hg^{\cdot}$ or η^5-$C_5H_5Cr(NO)_2^{\cdot}$, undergoes further abstraction of halogen by $Mn(CO)_5^{\cdot}$, coupling with the $Mn(CO)_5^{\cdot}$ or ligand substitution. Isolated metal-containing products include SnI_2, Cu, $Mn(CO)_5HgX$, Hg, $[Mn(CO)_5]_2Hg$ and η^5-$C_5H_5Cr(CO)_2NO$. Photolysis of $Mn_2(CO)_{10}$ in the presence of each of the metal—metal bonded compounds, $(\eta^5$-$C_5H_5)_2Cr_2(NO)_4$ and $[Co_2(CNCH_3)_{10}](BF_4)_4$, does not give the respective heterodinuclear combinations, $(\eta^5$-$C_5H_5)(NO)_2CrMn(CO)_5$ and $[(CH_3NC)_5$-$CoMn(CO)_5]^{2+}$, as detectable or isolable species; instead, η^5-$C_5H_5Cr(CO)_2NO$, $Mn(CO)_4NO$, $Mn_2(CO)_9CNCH_3$, and $[Mn(CO)(CNCH_3)_5]^+$ are among the isolated products. The photoreaction between $Mn_2(CO)_{10}$ and CH_3I provides a convenient synthesis of $Mn(CO)_5I$.

Introduction

In 1970, Gray and co-workers [1] assigned the absorption at 29400 cm^{-1} (340 nm) in the electronic spectrum of $Mn_2(CO)_{10}$ to a transition between the Mn—Mn σ-bonding orbital and the corresponding antibonding orbital. This assignment prompted a number of photochemical investigations on di- and poly-nuclear metal carbonyl complexes with a view to inducing cleavage of the metal—metal bond. Complexes cleaved in this manner include $Mn_2(CO)_{10}$ [2—7], $Re_2(CO)_{10}$ [3,8], $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ [9—11], $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ [9,12], $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ [11,13], $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4$ [13] and $Ru_3(CO)_{12}$ [14], as well as a variety of heterodinuclear metal carbonyls [3,15—18], homodinuclear substituted metal carbonyls [3,19,20] and non-carbonyl species with metal—metal multiple bonds [21].

In the course of our studies of the photochemistry of $Mn_2(CO)_{10}$ in THF, we observed the formation of a paramagnetic species with a six-line ESR spectrum [2]. The nature of this species created much controversy [22,23] before finally being settled as high-spin $[Mn(THF)_6]^{2+}$ with $[Mn(CO)_5]^-$ as the counterion [6,24]. The $Mn(CO)_5^{\cdot}$ radical, originally thought to be responsible for the observed ESR spectrum [2], was subsequently shown to be a short-lived entity [3] with a large rate constant for recombination even in such donor solvents as THF and ethanol [7,25]. Recently, its electronic spectrum was measured [25]. This radical, which readily dissociates CO [26], is considered to be part of a sequence of reactions leading to the formation of $[Mn(THF)_6]^{2+}$ in the photolysis of $Mn_2(CO)_{10}$ [4,6]. However, mechanistic details of the disproportionation to manganese(II) and (—I) remain unknown.

Although, as indicated above, the "controversial paramagnetic species" generated during photolysis of $Mn_2(CO)_{10}$ in THF has been accorded much attention, there appears little doubt that the initial photoproduct is $Mn(CO)_5^{\cdot}$ [4,6,7]. In this paper, we report on photochemically induced reactions of $Mn_2(CO)_{10}$ with each of iodine, organic and inorganic halides, and organometallic compounds in several organic solvents, including THF. The formation of the observed products generally implicates the $Mn(CO)_5^{\cdot}$ radical as the reactive manganese carbonyl species. Some reactions provide improved methods of synthesis of previously reported compounds.

Experimental

Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ESR spectra were measured in a Scanco S-812 flat cell on a Varian V4500-10A spectrometer using a V-4560 100 KHz modulating unit and a V4250-A sweep unit. UV-visible spectra were recorded on a Cary 14 spectrophotometer. Proton NMR spectra were taken on a Varian Associates A-60A spectrometer using tetramethylsilane (TMS) as an internal standard. IR measurements were made on a Perkin—Elmer Model 337 or Beckman IR-9 spectrophotometer using polystyrene film for calibration. Raman spectra were recorded on a Jarrell-Ash 25-300 Raman spectrometer employing a Spectra Physics 261 exciter and a Czerny-Turner scanning double monochromator. Mass spectra (MS) were taken by Mr. C.R. Weisenberger on an AEI Model MS-9 spectrometer at 70 eV. Analysis of gaseous mixtures was conducted by GC-MS using a duPont Model 21-490 mass spectrometer interfaced with a Perkin-Elmer Model 990 gas chromatograph. Elemental analyses were obtained commercially by Galbraith Laboratories, Inc., Knoxville, Tenn., and Pascher Mikroanalytisches Laboratorium, Bonn, West Germany. Manganese was determined in this laboratory by oxidation to permanganate [27], whereas CO was measured manometrically after oxidation of the metal carbonyl with excess I_2 or

$(NH_4)_2[Ce(NO_3)_6]$ (with an added trace of OsO_4).

Unless otherwise indicated, Ventron acid alumina, deactivated with distilled water (6%), was used in chromatographic separations and purifications. Carbon monoxide (Air Products, Research Grade) and N_2 (Liquid Carbonic, Prepurified) used to blanket the reaction solutions were dried by passage through concentrated H_2SO_4 and a column packed with P_4O_{10}. Argon (Burdette, Prepurified) and He (Burdette, CP Grade) were used as received. Reagent grade solvents were distilled directly into the reaction vessel under an appropriate gaseous atmosphere. The following solvents were purified further before distillation. THF was refluxed for at least 3 days over $LiAlH_4$ under Ar and then distilled. Benzene was refluxed for 24 h over CaH_2 and distilled before use, collecting only the fraction boiling over 80°C. Cyclohexane, hexane and heptane were stirred over 40% fuming H_2SO_4 for 3 days. The organic layer was then washed with three portions of each 0.1 M KOH and water, dried over Drierite for 2 days and fractionated from CaH_2 through a 30 cm Vigreux column. Pentane was distilled from CaH_2 and stored over molecular sieves (Linde, 4A).

Reagents

Decacarbonyldimanganese, from Strem Chemical Co., was sublimed at 40—50°C under reduced pressure before use. Iodine was sublimed twice. Other commercially procured chemicals were of reagent grade quality and were used as received. ^{13}CO, from Merck, Sharp and Dohme, was 91 mol %.

The compounds C_6H_5HgI [28], SnI_4[29], η^5-$C_5H_5Cr(NO)_2Cl$ [30] and $(\eta^5$-$C_5H_5)_2Cr_2(NO)_4$ [31] were prepared by literature procedures. $[Co_2(CNCH_3)_{10}](BF_4)_4$ was synthesized by the general method of Sacco for the perchlorate salt [32].

Photolysis procedures

The source of near ultraviolet radiation for all photoreactions in this study was a merry-go-round Rayonet Model RPR-100 photochemical reactor equipped with sixteen 350 nm lamps. Reactions were conducted in 20, 100 or 350 cm^3 pyrex tubes. Solutions to be irradiated were prepared using degassed solvents; they were either hermetically sealed under N_2, Ar, He or CO, or maintained under a steady flow of one of these gases. All photoreactions were conducted at room temperature. Analysis of photolyzed solutions was performed by IR spectroscopy in the 2300 to 1600 cm^{-1} region. Lamp intensities for quantum yield measurements were determined using ferrioxalate actinometry [33].

Reaction of $Mn_2(CO)_{10}$ with I_2 in cyclohexane

Experimental conditions for this reaction varied, but generally the procedure was as described below. Product identification was made by IR spectroscopy in the $\nu(C{\equiv}O)$ region utilizing literature data for $Mn_2(CO)_{10}$ [34], $Mn(CO)_5I$ [35] and $Mn_2(CO)_8I_2$ [35].

A solution of $Mn_2(CO)_{10}$ and I_2 in cyclohexane was irradiated under N_2 for different lengths of time. The mixture was then evaporated to dryness on a rotary evaporator to give an orange solid. Sublimation (~25°C, 0.001 Torr) afforded red-orange and yellow crystals and a brown residue. The sublimate was dissolved in minimum hexane and chromatographed on alumina. Elution with hexane gave first a yellow band of $Mn_2(CO)_{10}$ and then an orange band of $Mn(CO)_5I$.

The brown residue was treated with benzene and the resulting mixture was filtered to give a white powder, characterized as MnI_2 (e.g., no IR absorptions over the 4000 to 400 cm^{-1} region; m.p. 78—80°C (dec.), lit. [36] m.p. ~80°C (dec.)). The orange-brown filtrate was cooled at 0°C to yield brown crystals of $Mn_2(CO)_8I_2$, which were collected on a filter, washed with pentane and dried. The filtrate was evaporated to dryness and the residue was sublimed (~25°C, 0.001 Torr) to furnish additional $Mn(CO)_5I$.

Reaction of $Mn_2(CO)_{10}$ with I_2 in THF under CO

A solution of $Mn_2(CO)_{10}$ (0.393 g, 1.01 mmol) and I_2 (0.255 g, 1.01 mmol) in 100 cm^3 of THF under CO was irradiated for 10 min, during which time it turned from yellow to red-orange. The THF was removed, the residue was dissolved in 50 cm^3 of hexane and the resulting solution was chromatographed. Three bands were developed. The first, yellow, was eluted off with hexane to give 0.165 g of unreacted $Mn_2(CO)_{10}$. The second, orange, also eluted off with hexane, gave 0.230 g (62% yield based on reacted $Mn_2(CO)_{10}$) of $Mn(CO)_5I$. The third band was eluted off with $CHCl_3$ to give unreacted I_2.

Reaction of $Mn_2(CO)_{10}$ with CH_3I

Irradiation of a solution of $Mn_2(CO)_{10}$ (0.242 g, 0.620 mmol) and CH_3I (0.762 g, 5.37 mmol) in 20 cm^3 of cyclohexane under N_2 for 1 h resulted in the evolution of large amounts of gas (shown by GC-MS to be a mixture of CO, CH_4 and C_2H_6) and the deposition of a white solid (identified as MnI_2). The resulting red-orange solution was analyzed as described above to afford a small amount of unreacted $Mn_2(CO)_{10}$ and 0.140 g (70% yield based on reacted $Mn_2(CO)_{10}$) of $Mn(CO)_5I$.

Reaction of $Mn_2(CO)_{10}$ with SnI_4

A solution of $Mn_2(CO)_{10}$ (0.785 g, 2.01 mmol) and SnI_4 (1.25 g, 2.00 mmol) in 100 cm^3 of THF under CO was irradiated for 1 h. The resulting red-orange solution was decanted from a small amount of insoluble material and evaporated to dryness. The residue was washed with hexane to give a clear orange filtrate and a yellow solid. This hexane-insoluble solid was washed with CH_2Cl_2 to yield a yellow solution and a yellow-orange residue. The hexane washings were concentrated and chromatographed on alumina to afford 0.126 g of unreacted $Mn_2(CO)_{10}$ and 0.967 g of $Mn(CO)_5I$. Chromatography on alumina of the CH_2Cl_2 washings, eluting with CH_2Cl_2, gave a small amount of $Mn_2(CO)_8I_2$.

The yellow-orange CH_2Cl_2-insoluble solid showed no IR absorptions over the 4000 to 400 cm^{-1} region, m.p. 320°C (for SnI_2, m.p. 320°C [37]). Yield 0.464 g.

Reaction of $Mn_2(CO)_{10}$ with $CuCl_2 \cdot 2\,H_2O$

To a solution of $CuCl_2 \cdot 2\,H_2O$ (0.174 g, 1.01 mmol) in 100 cm^3 of THF under CO was added solid $Mn_2(CO)_{10}$ (0.190 g, 0.480 mmol) and, after complete dissolution, the reaction mixture was irradiated under a flow of CO. Progress of the reaction was followed by monitoring the $\nu(C\equiv O)$ region of the

IR spectrum. After 5 min, about 50% of the $Mn_2(CO)_{10}$ was left and $Mn(CO)_5Cl$ [35] was clearly discernible. Further photolysis (additional 10 min) resulted in the deposition of metallic copper on the inner walls of the reaction flask. At this point the solution was filtered to give a clear yellow filtrate, from which a white precipitate gradually settled out. After an additional filtration, the solvent was removed under reduced pressure and the resulting yellow residue was dissolved in 1/1 hexane/benzene. An IR spectrum of this solution showed the presence of substantial amounts of $Mn(CO)_5Cl$ and $Mn_2(CO)_8Cl_2$ [35], but little, if any, $Mn_2(CO)_{10}$.

The white non-carbonyl powder was soluble in warm water. Aqueous solutions gave a six-line ESR spectrum with a separation of ca. 110 G.

Reaction of $Mn_2(CO)_{10}$ with HgX_2 (X = Cl, Br or I)

The reaction with HgI_2 was typical and will be described in detail. A solution of $Mn_2(CO)_{10}$ (0.503 g, 1.29 mmol) and HgI_2 (0.580 g, 1.28 mmol) in 100 cm^3 of THF was maintained under CO for 1.5 h. No changes were observed in the IR spectrum. The solution was then irradiated for 1 h, resulting in the formation of a small amount of metallic mercury. The orange solution was decanted from the mercury and evaporated to dryness. The resulting solid was washed with four 10 cm^3 portions of hexane to give an orange solution and a yellow residue. The hexane washings were chromatographed on alumina to yield 0.102 g of $Mn_2(CO)_{10}$ and 0.262 g of $Mn(CO)_5I$. The yellow residue was dissolved in CH_2Cl_2 and also chromatographed. Elution with acetone afforded 0.533 g of a lemon yellow solid, m.p. 136—137°C (lit. [38] m.p. 136°C), showing IR $\nu(C{\equiv}O)$ bands at 2104, 2041 and 2016 cm^{-1} in CH_2Cl_2 solution, in agreement with the spectrum reported [39] for $Mn(CO)_5HgI$.

Similar results were obtained with $HgBr_2$ and $HgCl_2$. The irradiation times were 1.5 h, and minimum yields of $Mn(CO)_5HgX$ (X = Br, Cl) were 50%. Unlike $Mn(CO)_5HgI$, these compounds lacked sufficient solubility for chromatography, and were recrystallized instead. Characterization was accomplished by comparison of the melting points (175—177 and 182—183°C for X = Br and Cl, respectively) and IR $\nu(C{\equiv}O)$ spectra with those reported in the literature [38,39]. In the reaction with $HgCl_2$, $Mn_2(CO)_8Cl_2$ was isolated instead of $Mn(CO)_5Cl$.

Reaction of $Mn_2(CO)_{10}$ with C_6H_5HgI

In 300 cm^3 of THF was dissolved C_6H_5HgI (1.06 g, 2.65 mmol) under CO with the aid of gentle heating. When the solution had cooled to 30°C, $Mn_2(CO)_{10}$ (1.17 g, 3.00 mmol) was added and, after dissolution, the mixture was stored for 1 h. No changes were observed in the IR spectrum. Irradiation for 2 h followed to give a clear orange solution, from which solvent was removed under reduced pressure. The residue was extracted with hexane until the extracts were colorless, giving an orange solution and a yellow solid. Chromatography on alumina of the extracts as described earlier afforded 0.433 g of $Mn_2(CO)_{10}$ and 0.281 g of $Mn(CO)_5I$. Then, development of the same column with benzene gave a colorless effluent, from which 0.387 g of white crystals was obtained upon evaporation to dryness, m.p. 121—122°C (for $Hg(C_6H_5)_2$, m.p. 121.8°C [40]). The MS (at 100°C) of the solid agreed well with that reported [41] for $Hg(C_6H_5)_2$, showing the parent ion multiplet at m/e 586– 594 with the expected isotopic distribution pattern for a monomercury complex.

The yellow solid from the extraction during work up was washed with 30 cm^3 of THF to give a yellow solution and leave 0.296 g of undissolved material. This yellow residue was shown to be $[Mn(CO)_5]_2Hg$ by comparison of its IR $\nu(C\equiv O)$ and Raman spectra and its mass spectrum (at 150°C) with the corresponding data from the literature [42—44].

The yellow washings were evaporated to dryness and the resulting solid gave an IR spectrum consistent with the presence of a mixture of C_6H_5HgI and $[Mn(CO)_5]_2Hg$.

Reaction of $Mn_2(CO)_{10}$ with η^5-$C_5H_5Cr(NO)_2Cl$

A solution of $Mn_2(CO)_{10}$ (0.397 g, 1.02 mmol) and η^5-$C_5H_5Cr(NO)_2Cl$ (0.212 g, 1.00 mmol) in 100 cm^3 of THF under CO was irradiated for 0.5 h, during which time it changed color from green to purple. At this point the presence of $Mn(CO)_5Cl$ and $(\eta^5$-$C_5H_5)_2Cr_2(NO)_4$ was apparent in the IR spectrum of the reaction mixture. Solvent was removed and the residue was dissolved in 20 cm^3 of benzene. Chromatography on activated neutral alumina resulted in the appearance of three bands. The first two, yellow and orange, were eluted off together with benzene and gave, after removal of the solvent, small amounts of $Mn_2(CO)_{10}$ and η^5-$C_5H_5Cr(CO)_2NO$, the latter being characterized by its IR $\nu(C\equiv O)$ and $\nu(N\equiv O)$ absorptions at 2026s, 1958s and 1719s cm^{-1} in hexane solution [45]. The third benzene-eluted band, purple, afforded a deep blue-black solid upon removal of the solvent under reduced pressure. This solid was shown by its IR $\nu(N\equiv O)$ absorptions at 1676vs and 1522m cm^{-1} in $CHCl_3$ solution to be $(\eta^5$-$C_5H_5)_2Cr_2(NO)_4$ [31]. Yield ca. 40% based on η^5-$C_5H_5Cr(NO)_2Cl$.

Reaction of $Mn_2(CO)_{10}$ with $(\eta^5$-$C_5H_5)_2Cr_2(NO)_4$

In 100 cm^3 of heptane were dissolved $Mn_2(CO)_{10}$ (0.0390 g, 0.100 mmol) and $(\eta^5$-$C_5H_5)_2Cr_2(NO)_4$ (0.0354 g, 0.100 mmol), and the resulting solution was stored under CO for 1 h. No reaction was detected by IR spectroscopy. The solution was then irradiated until the starting materials were almost completely consumed (ca. 2 h). Chromatography on alumina of the reaction mixture, eluting with hexane, first afforded $Mn_2(CO)_{10}$ and then 0.105 g of the orange η^5-$C_5H_5Cr(CO)_2NO$, m.p. 65—66°C (lit. [45] m.p. 67°C), IR and ^1H NMR spectra in agreement with those reported [45], and the MS (at 150°C) showing the parent ion multiplet at m/e 201—206 with the expected isotopic distribution pattern for a monochromium compound (calculated from isotopic percentages [46]).

When the same photoreaction was conducted in THF, additional absorptions were observed in the IR $\nu(C\equiv O)$ and $\nu(N\equiv O)$ regions at the conclusion of the photolysis. The reaction mixture was then fractionated through 0, —35, - 78 and —196°C traps. The orange liquid collected in the —35°C trap was shown by IR spectroscopy ($\nu(C\equiv O)$ and $\nu(N\equiv O)$ bands at 2102m, 2029s, 1982s and 1754m cm^{-1}) to be $Mn(CO)_4NO$ [47].

Reaction of $(\eta^5$-$C_5H_5)_2Cr_2(NO)_4$ with CO

A solution of $(\eta^5$-$C_5H_5)_2Cr_2(NO)_4$ (0.02 g) in 100 cm^3 of heptane under CO was photolyzed until the nitrosyl complex was consumed (disappearance of IR ν(N≡O) at 1672 cm^{-1}, ca. 45 min). The reaction mixture was then filtered to give an orange solution and a brown solid. The filtrate was found by IR spectroscopy to contain η^5-$C_5H_5Cr(CO)_2NO$.

The brown solid was extracted with 20 cm^3 of benzene through a frit, and the extract was treated with 40 cm^3 of heptane and stored at ca. 0°C. The resulting brown microcrystalline precipitate was isolated by decanting the mother liquor and was washed with pentane. The yield of this material was sufficient only for an IR spectrum (as KBr pellet): 3100w, 1815ms, 1705s, 1640s, 1435mw, 1400m, 1385m, 1125w, 1070w, 1015m and 810ms cm^{-1}.

Reaction of $Mn_2(CO)_{10}$ with $[Co_2(CNCH_3)_{10}](BF_4)_4$

A suspension of $[Co_2(CNCH_3)_{10}](BF_4)_4$ (0.0810 g, 0.0930 mmol) in 100 cm^3 of THF containing dissolved $Mn_2(CO)_{10}$ (0.0919 g, 0.235 mmol) under CO was photolyzed with magnetic stirring. After 0.5 h the mixture was filtered to give 0.0700 g of a red crystalline solid, shown by IR spectroscopy to be unreacted $[Co_2(CNCH_3)_{10}](BF_4)_4$, and an orange solution. The solution was evaporated to dryness, the residue was extracted with hexane and the extract was chromatographed on alumina. Two yellow bands were eluted off with hexane; they gave respectively 0.0784 g of $Mn_2(CO)_{10}$ and ca. 0.02 g of yellow-orange crystals, m.p. 92—93°C (dec.), characterized by IR spectroscopy (ν(C≡N) and ν(C≡O) bands at 2186w, 2088w, 2028m, 1997s, 1972mw and 1962m cm^{-1} in hexane solution) and mass spectrometry (at 80°C, parent ion peak at *m/e* 402) as $Mn_2(CO)_9CNCH_3$. A small brown band remained at the top of the column and could not be eluted off even with acetone.

The above reaction was also conducted in methanol. In 300 cm^3 of methanol was dissolved $[Co_2(CNCH_3)_{10}](BF_4)_4$ (0.263 g, 0.289 mmol) under CO with the aid of gentle heating. When the blue solution had cooled to 30°C, solid $Mn_2(CO)_{10}$ (0.278 g, 0.712 mmol) was added and, after dissolution, the resulting green solution was irradiated under CO for 5 min, changing color to yellow-orange. After addition of $Na[B(C_6H_5)_4]$ and stirring for ca. 3 min, the volume of the solution was reduced to 150 cm^3. Filtration afforded a pale yellow solid (0.200 g) and an orange solution.

The solid was recrystallized by dissolution in 10 cm^3 of acetone, filtration, addition of 10 cm^3 of methanol and another filtration. The filtrate was concentrated under reduced pressure to yield white crystals, which were washed with 10 cm^3 of cold (0°C) methanol and 50 cm^3 of pentane, and dried (0.001 Torr) for 1 h. Further recrystallization to yield long white needles (0.040 g) was effected by dissolution of this material in boiling methanol under Ar and cooling at 0°C.

Anal.: Found: C, 68.19; H, 5.86; B, 1.80; Mn, 8.41; N, 10.89. $C_{35}H_{35}BMnN_5O$ calcd.: C, 69.22; H, 5.82; B, 1.78; Mn, 9.04; N, 11.53. IR (2300 to 1800 cm^{-1}): 2228w, 2184w, 2154vs, 2015w(br), 1970(sh) and 1959m cm^{-1} in CH_2Cl_2 solution. ^{1}H NMR τ 2.50—3.20m (20 H) and 6.68s (15 H) in CD_3COCD_3 solution.

The orange solution from the above filtration was evaporated to dryness and the residue was washed with hexane until the washings were colorless. The resulting orange solution was chromatographed as before to yield 0.1 g of $Mn_2(CO)_{10}$ and 0.020 g $Mn_2(CO)_9CNCH_3$. The insoluble material was washed with CH_2Cl_2 on a frit, leaving an off-white solid (A). Evaporation of the washings yielded (0.05 g) another off-white material (B).

Solid A showed IR bands characteristic of the anions BF_4^- and $[B(C_6H_5)_4]^-$, but no $\nu(C\equiv O)$ or $\nu(C\equiv N)$ absorptions. The presence of cobalt therein was established qualitatively according to Vogel [48]. Solid B was recrystallized in the same manner as the $[Mn(CO)(CNCH_3)_5][B(C_6H_5)_4]$ above to furnish 0.02 g of white crystals. IR (2300 to 1800 cm^{-1}): 2238w, 2216w, 2181s, 2154(sh), 2066w, 2007s and 1966s cm^{-1} as KBr pellet. Insufficient material was available for elemental analysis.

The reaction between $Mn_2(CO)_{10}$ and $[Co_2(CNCH_3)_{10}](BF_4)_4$ in methanol was run also under He. The identified products were the same as those obtained in the corresponding photoreaction under CO.

Results and discussion

Reaction of $Mn_2(CO)_{10}$ with I_2

Solutions of $Mn_2(CO)_{10}$ and I_2 in cyclohexane under N_2 undergo no detectable chemical change in the dark for at least 2 h. By contrast, photolysis (at 350 nm) results in the evolution of a gas and formation of $Mn(CO)_5I$, $Mn_2(CO)_8I_2$ and MnI_2. The gas was not identified, but is almost certainly CO.

Relative concentrations of the manganese carbonyls in a photolyzed cyclohexane solution of $Mn_2(CO)_{10}$ and excess I_2 under N_2 were measured by IR spectroscopy as a function of time. For these measurements, Beer's law plots of the intensities of the absorption bands at 2125, 2087 and 1985 cm^{-1} of $Mn(CO)_5I$, $Mn_2(CO)_8I_2$ and $Mn_2(CO)_{10}$, respectively, were employed, after their linearity in the appropriate concentration range had been demonstrated. The results are plotted in Fig. 1. It is readily seen that the concentration of

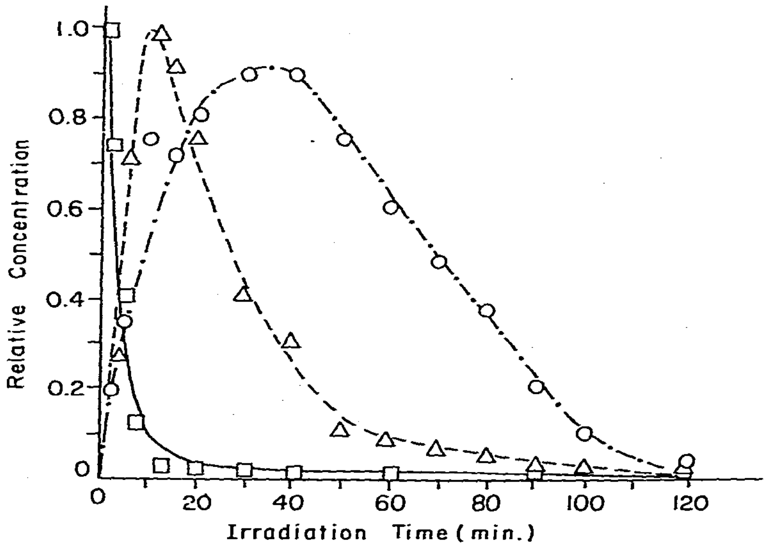

Fig. 1. Relative concentrations of $Mn_2(CO)_{10}$ (□), $Mn(CO)_5I$ (△) and $Mn_2(CO)_8I_2$ (○) during photolysis of $Mn_2(CO)_{10}$ (2.90×10^{-3} M) and I_2 (3.28×10^{-2} M) in cyclohexane.

$Mn(CO)_5I$ reaches a maximum early during the photolysis, whereas that of $Mn_2(CO)_8I_2$ attains its peak considerably later.

To ascertain whether the $Mn_2(CO)_8I_2$ derives from photolysis of $Mn(CO)_5I$, a solution of the latter manganese carbonyl in cyclohexane under N_2 was irradiated for 0.5 h. Only unreacted $Mn(CO)_5I$ and a trace of $Mn_2(CO)_{10}$ were detected by IR spectroscopy. By contrast, irradiation under N_2 for 0.5 h of a cyclohexane solution of $Mn(CO)_5I$ (3.10×10^{-2} M) and I_2 (7.0×10^{-3} M) resulted in a vigorous evolution of CO and the formation of $Mn_2(CO)_8I_2$ and MnI_2. There was no observable reaction in the dark. In another control experiment, $Mn_2(CO)_8I_2$ in cyclohexane under N_2 was irradiated for 2 h. The photoproducts were identified as $Mn_2(CO)_{10}$ and MnI_2. Similar results have been reported by Bamford and co-workers [49] for photolysis of $Mn(CO)_5X$ (X = Cl, Br) alone in benzene and of $Mn_2(CO)_8X_2$ (X = Cl or Br) in benzene or cyclohexane.

These observations may be accounted for by the following sequence of reactions (eqs. 1—4):

$$Mn_2(CO)_{10} \overset{h\nu}{\rightleftharpoons} 2\ Mn(CO)_5^{\cdot} \tag{1}$$

$$2\ Mn(CO)_5^{\cdot} + I_2 \rightarrow 2\ Mn(CO)_5I \tag{2}$$

$$2\ Mn(CO)_5I \xrightleftharpoons{h\nu,\ I_2} Mn_2(CO)_8I_2 + 2\ CO \tag{3}$$

$$2\ Mn_2(CO)_8I_2 \xrightarrow{h\nu} Mn_2(CO)_{10} + 2\ MnI_2 + 6\ CO \tag{4}$$

That these transformations are initiated by a photochemical activation of $Mn_2(CO)_{10}$ rather than I_2 has been already demonstrated [3]. It is unlikely that the $Mn_2(CO)_8I_2$ derives in a significant quantity from $Mn_2(CO)_{10}$ and I_2, as the concentration of $Mn_2(CO)_{10}$ is very low when $Mn_2(CO)_8I_2$ begins to build up (see Fig. 1). The principal source of $Mn_2(CO)_8I_2$ seems to be $Mn(CO)_5I$. The role of I_2 in promoting this photoreaction (eq. 3) is unknown, but its presence is necessary.

Photolysis of $Mn_2(CO)_{10}$ and I_2 was also carried out in THF under CO. Only $Mn(CO)_5I$ and unreacted $Mn_2(CO)_{10}$ were isolated after short irradiation times. No $Mn_2(CO)_8I_2$ could be detected. The quantum yield for the disappearance of $Mn_2(CO)_{10}$, $\phi_{-Mn_2(CO)_{10}} = 0.47 \pm 0.09$ was found to be nearly the same as that reported [3] for the reactions of $Mn_2(CO)_{10}$ with I_2 in cyclohexane ($\phi_{-Mn_2(CO)_{10}} = 0.4$) and with neat CCl_4 ($\phi_{-Mn_2(CO)_{10}} = 0.41$ and 0.48 at 366 and 313 nm, respectively). The similarity in the disappearance quantum yields for $Mn_2(CO)_{10}$ in all three reactions strongly supports the common pathway of homolysis of the Mn—Mn bond to produce $Mn(CO)_5^{\cdot}$.

Reaction of $Mn_2(CO)_{10}$ with CH_3I

Irradiation of $Mn_2(CO)_{10}$ and excess CH_3I in cyclohexane under N_2 proceeds as in eq. 5.

$$Mn_2(CO)_{10} + CH_3I \xrightarrow{h\nu} Mn(CO)_5I + MnI_2 + CO + CH_4 + C_2H_6 \tag{5}$$

No $Mn(CO)_5CH_3$ was detected. This photoreaction is therefore strictly analogous to that observed between $Mn_2(CO)_{10}$ and $C_6H_5CH_2Cl$ [3], and points to a radical, rather than anionic, nature of the reacting $Mn(CO)_5$ fragment. The high yield (ca. 70%), coupled with the ease of separation and purification, make this an attractive synthetic procedure for $Mn(CO)_5I$.

Reaction of $Mn_2(CO)_{10}$ with SnI_4

Tin(IV) iodide and $Mn_2(CO)_{10}$ undergo the following net photoreaction in THF under CO (eq. 6).

$$Mn_2(CO)_{10} + SnI_4 \xrightarrow[CO]{h\nu} 2\ Mn(CO)_5I + SnI_2 \qquad (6)$$

In addition, a small quantity of $Mn_2(CO)_8I_2$ is produced. Although the source of the octacarbonyl is unknown, it is entirely possible that this compound results from a photochemical reaction of $Mn(CO)_5I$ in the presence of SnI_4, as it does from a similar reaction in the presence of I_2 (vide supra).

The quantum yield for the disappearance of $Mn_2(CO)_{10}$, $\phi_{-Mn_2(CO)_{10}} = 0.36 \pm 0.04$, is approximately half of that for the appearance of $Mn(CO)_5I$, $\phi_{+Mn(CO)_5I} = 0.64 \pm 0.06$. This points again to a photochemically induced homolytic cleavage of the Mn—Mn bond. The $Mn(CO)_5^{\cdot}$ radical then abstracts iodine from SnI_4 (eq. 7),

$$Mn(CO)_5^{\cdot} + SnI_4 \rightarrow Mn(CO)_5I + SnI_3^{\cdot} \qquad (7)$$

The formation of SnI_2 may occur either by reaction of $SnI_3^{\cdot}$ with $Mn(CO)_5^{\cdot}$ to give $Mn(CO)_5SnI_3$ which under irradiation decomposes to $Mn(CO)_5I$ and SnI_2, or by abstraction of iodine from $SnI_3^{\cdot}$ by $Mn(CO)_5^{\cdot}$ also to give $Mn(CO)_5I$ and SnI_2. The former process would be analogous to the photochemical decomposition of $Mn(CO)_5HgX$ (X = Cl, Br, I) to yield $Mn(CO)_5X$ and Hg (vide infra).

Reaction of $Mn_2(CO)_{10}$ with $CuCl_2 \cdot 2\ H_2O$

Photolysis of $Mn_2(CO)_{10}$ and excess $CuCl_2 \cdot 2\ H_2O$ in THF under CO affords $Mn(CO)_5Cl$, $Mn_2(CO)_8Cl_2$, metallic Cu, and $MnCl_2$ (probably hydrated). The quantum yield for the disappearance of $Mn_2(CO)_{10}$, $\phi_{-Mn_2(CO)_{10}} = 0.4$, again suggests the formation of $Mn(CO)_5^{\cdot}$ which readily abstracts chlorine from $CuCl_2 \cdot 2\ H_2O$ to produce $Mn(CO)_5Cl$ and CuCl. Loss of chlorine by the CuCl to $Mn(CO)_5^{\cdot}$ would then afford metallic Cu and additional $Mn(CO)_5Cl$. The observed formation of $MnCl_2$ may be ascribed to photochemical decomposition of $Mn_2(CO)_8Cl_2$ [49].

Reaction of $Mn_2(CO)_{10}$ with HgX_2 (X = Cl, Br or I)

Photochemical reaction of $Mn_2(CO)_{10}$ with HgX_2 (X = Cl, Br or I) in THF under CO for 1—1.5 h proceeds to the products $Mn(CO)_5X$ (or $Mn_2(CO)_8X_2$, when X = Cl), $Mn(CO)_5HgX$ and metallic Hg. There is no reaction in the dark. The origin of Hg was established by independent photolysis experiments on $Mn(CO)_5HgX$ (X = Cl, Br, I) in THF under CO. In all three cases, the formation of $Mn(CO)_5X$ in solution and separation of metallic Hg were observed in the course of the irradiation. Thus it appears that the initial photoreaction between $Mn_2(CO)_{10}$ and HgX_2 proceeds as in eq. 8,

$$Mn_2(CO)_{10} + HgX_2 \xrightarrow[CO]{h\nu} Mn(CO)_5X + Mn(CO)_5HgX \tag{8}$$

and is followed by (eq. 9)

$$Mn(CO)_5HgX \xrightarrow[CO]{h\nu} Mn(CO)_5X + Hg \tag{9}$$

The quantum yield for the disappearance of $Mn_2(CO)_{10}$, $\phi_{-Mn_2(CO)_{10}} = 0.13 \pm 0.01$, is the same for all three mercury(II) halides, but is substantially lower than for the photoreaction with I_2, SnI_4 or $CuCl_2 \cdot 2\ H_2O$. It strongly points to a photochemical excitation of $Mn_2(CO)_{10}$ rather than HgX_2. In fact, each of the three HgX_2 compounds was recovered unchanged after photolysis in THF under CO for 0.5 h. The quantum yields for the formation of $Mn(CO)_5I$ and $Mn(CO)_5HgI$, $\phi_{+Mn(CO)_5I} = 0.10 \pm 0.01$ and $\phi_{+Mn(CO)_5HgI} = 0.13 \pm 0.01$, are essentially identical with that for the consumption of $Mn_2(CO)_{10}$.

The above results again implicate homolytic cleavage of the Mn—Mn bond with the formation of $Mn(CO)_5^{\cdot}$. These radicals then abstract halogen from HgX_2 to give $Mn(CO)_5X$ and $HgX^{\cdot}$. The latter species apparently combine with $Mn(CO)_5^{\cdot}$ instead of undergoing dimerization to Hg_2X_2. The formation of $Mn_2(CO)_8Cl_2$ may possibly result from a photochemical reaction of $Mn(CO)_5Cl$ in the presence of $HgCl_2$ (vide supra).

Reaction of $Mn_2(CO)_{10}$ with C_6H_5HgI

There is no observable reaction between $Mn_2(CO)_{10}$ and C_6H_5HgI in THF under CO for 1 h in the dark. By contrast, photolysis of the above solution for 2 h produces $Mn(CO)_5I$, $[Mn(CO)_5]_2Hg$ and $Hg(C_6H_5)_2$, the overall process being that in eq. 10.

$$2\ Mn_2(CO)_{10} + 2\ C_6H_5HgI \xrightarrow[CO]{h\nu} 2\ Mn(CO)_5I + [Mn(CO)_5]_2Hg + Hg(C_6H_5)_2 \tag{10}$$

The formation of these products likely proceeds in two steps (eqs. 11 and 12), first

$$Mn_2(CO)_{10} + C_6H_5HgI \xrightarrow[CO]{h\nu} Mn(CO)_5I + Mn(CO)_5HgC_6H_5 \tag{11}$$

via reaction of $Mn(CO)_5^{\cdot}$ with C_6H_5HgI and with $C_6H_5Hg^{\cdot}$, and then

$$2\ Mn(CO)_5HgC_6H_5 \rightarrow [Mn(CO)_5]_2Hg + Hg(C_6H_5)_2 \tag{12}$$

The species $Mn(CO)_5HgC_6H_5$ has never been isolated, but it has been postulated [38] to account for the formation of $[Mn(CO)_5]_2Hg$ and HgR_2 in the reaction of various RHgOH complexes with $[Mn(CO)_5]^-$.

Work-up of the reaction mixture from photolysis in eq. 10 resulted in the isolation of a THF-soluble material which was shown by IR spectroscopy to be C_6H_5HgI and $[Mn(CO)_5]_2Hg$ in the solid. In CH_2Cl_2 solution, however, the IR spectrum in the $\nu(C{\equiv}O)$ region of this material gradually changed to that of $Mn(CO)_5HgI$. In THF, the observed change is similar, but more rapid. As a result of these observations, a reaction was conducted in the dark between $[Mn(CO)_5]_2$-Hg (5×10^{-5} M) and C_6H_5HgI (5×10^{-3} M) in CH_2Cl_2 at 25°C. After 20 min, a complete conversion to $Mn(CO)_5HgI$ was noted by IR spectroscopy. These results implicate the thermal equilibrium in eq. 13,

$$[\mathrm{Mn(CO)_5}]_2\mathrm{Hg} + 2\ \mathrm{C_6H_5HgI} \rightleftharpoons 2\ \mathrm{Mn(CO)_5HgI} + \mathrm{Hg(C_6H_5)_2} \qquad (13)$$

which is strictly analogous to that observed [50] for the molybdenum complexes (eq. 14),

$$[\eta^5\text{-}\mathrm{C_5H_5Mo(CO)_3}]_2\mathrm{Hg} + 2\ \mathrm{CH_3HgI} \rightleftharpoons 2\ \eta^5\text{-}\mathrm{C_5H_5Mo(CO)_3HgI} + \mathrm{Hg(CH_3)_2} \qquad (14)$$

It is of interest that the equilibrium in eq. 13 lies completely to the right in THF and CH_2Cl_2, but completely to the left in the solid state.

Reaction of $Mn_2(CO)_{10}$ with η^5-$C_5H_5Cr(NO)_2Cl$

In an attempt to synthesize unreported $(\eta^5\text{-}C_5H_5)(NO)_2CrMn(CO)_5$, $Mn_2(CO)_{10}$ and $\eta^5\text{-}C_5H_5Cr(NO)_2Cl$ in THF solution were irradiated under CO for 0.5 h. However, the desired $(\eta^5\text{-}C_5H_5)(NO)_2CrMn(CO)_5$ could not be detected by IR spectroscopy, the overall observable reaction being that in eq. 15,

$$\mathrm{Mn_2(CO)_{10}} + \eta^5\text{-}\mathrm{C_5H_5Cr(NO)_2Cl} \xrightarrow[\mathrm{CO}]{h\nu} \mathrm{Mn(CO)_5Cl} + (\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{Cr_2(NO)_4} + \eta^5\text{-}\mathrm{C_5H_5Cr(CO)_2NO} \qquad (15)$$

The formation of the above products may be rationalized in terms of the abstraction of chlorine from $\eta^5\text{-}C_5H_5Cr(NO)_2Cl$ by the photogenerated $Mn(CO)_5^{\cdot}$ radicals to yield $Mn(CO)_5Cl$ and $\eta^5\text{-}C_5H_5Cr(NO)_2^{\cdot}$. The latter radical then apparently undergoes dimerization rather than coupling with $Mn(CO)_5^{\cdot}$ under the photolytic conditions employed in this work. The other chromium-containing product, $\eta^5\text{-}C_5H_5Cr(CO)_2NO$, most likely arises from photolysis of $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_4$ under CO, perhaps via reaction of $\eta^5\text{-}C_5H_5Cr(NO)_2^{\cdot}$ with CO. It was shown in an independent experiment that irradiation of $(\eta^5\text{-}C_5H_5)_2\text{-}Cr_2(NO)_4$ under CO does indeed produce $\eta^5\text{-}C_5H_5Cr(CO)_2NO$.

Although the above method of synthesis of $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_4$ is convenient, the yield (ca. 40%) is not as high as that (56—75%) for the recently reported [51] reduction of $\eta^5\text{-}C_5H_5Cr(NO)_2Cl$ with zinc or sodium amalgam. This is because the photoreaction slows down considerably as the concentration of the strongly absorbing $(\eta^5\text{-}C_5H_5)_2Cr_2(NO)_4$ builds up with time.

Reaction of $Mn_2(CO)_{10}$ with $(\eta^5$-$C_5H_5)_2Cr_2(NO)_4$

Studies of Wrighton and co-workers [9,17] have shown that irradiation of a mixture of two homodinuclear metal carbonyls, $M_2(CO)_x$ and $M'_2(CO)_y$, produces their heterodinuclear combination, $MM'(CO)_{\frac{x+y}{2}}$. To prepare unknown $(\eta^5\text{-}C_5H_5)\text{-}(NO)_2CrMn(CO)_5$ by this general method, solutions of $Mn_2(CO)_{10}$ and $(\eta^5\text{-}C_5H_5)_2\text{-}Cr_2(NO)_4$ in heptane and in THF were photolyzed under CO, after it had been established that there is no observable reaction in the dark. However, as with the experiments on $Mn_2(CO)_{10}$ and $\eta^5\text{-}C_5H_5Cr(NO)_2Cl$, the desired compound could not be detected in the photolyzed reaction mixture. Instead, $\eta^5\text{-}C_5H_5Cr\text{-}(CO)_2NO$ and, in the case of the THF reaction, $Mn(CO)_4NO$ were first observed in the solution and then isolated.

Although admittedly speculative, a reasonable pathway for the formation of the two products may involve the generation and appropriate substitution reactions of the radicals η^5-$C_5H_5Cr(NO)_2^{\cdot}$ and $Mn(CO)_5^{\cdot}$. The radical η^5-$C_5H_5Cr(NO)_2^{\cdot}$ has been recently proposed [52] in photochemical studies on some η^5-cyclopentadienylnitrosylchromium complexes. In support of our suggested pathway is the independent formation of each of η^5-$C_5H_5Cr(CO)_2NO$ and $Mn(CO)_4NO$ by irradiation of $(\eta^5$-$C_5H_5)_2Cr_2(NO)_4$ under CO (vide supra) and of $Mn_2(CO)_{10}$ under NO [53], respectively. However, our inability to observe $(\eta^5$-$C_5H_5)(NO)_2CrMn(CO)_5$, the expected cross-coupling product of the two metal-centered radicals, is rather puzzling. Possibly, it may be a consequence of thermal or photochemical instability of this compound.

Reaction of $Mn_2(CO)_{10}$ with $[Co_2(CNCH_3)_{10}](BF_4)_4$

THF and methanol solutions of $Mn_2(CO)_{10}$ and $[Co_2(CNCH_3)_{10}](BF_4)_4$ were irradiated under CO with a view to synthesizing unknown $[(CH_3NC)_5CoMn(CO)_5]^{2+}$. The photolysis for 0.5 h in THF (in which the cobalt complex is only sparingly soluble) resulted in the isolation of unreacted starting materials and some $Mn_2(CO)_9CNCH_3$. The photolysis for 5 min in methanol (in which $[Co_2(CNCH_3)_{10}]^{4+}$ dissociates into $[Co(CNCH_3)_5^{\cdot}]^{2+}$ [32]), followed by the addition of $Na[B(C_6H_5)_4]$ and a lengthy work-up (see Experimental), afforded a number of products. Of these, $Mn_2(CO)_9CNCH_3$ and $[Mn(CO)(CNCH_3)_5][B(C_6H_5)_4]$ were separated and characterized. Another mixed carbonyl-methyl isocyanide complex, possibly of the type $[Mn(CO)_x(CNCH_3)_{6-x}][B(C_6H_5)_4]$, was obtained in too small a quantity for characterization. Its IR spectrum in the $\nu(C{\equiv}N)$—$\nu(C{\equiv}O)$ region did not sufficiently closely match the spectra reported by Treichel and co-workers for the different $[Mn(CO)_x(CNCH_3)_{6-x}]PF_6$ [54]. The complex $[Mn(CO)(CNCH_3)_5][B(C_6H_5)_4]$, characterized by elemental analysis and IR and ^{1}H NMR spectroscopy [54], was further identified as a monocarbonyl (or, possibly, a trans-dicarbonyl) by conducting the aforementioned photolysis in methanol with labeled $Mn_2(^{13}CO)(^{12}CO)_9$. Only one additional absorption band in the $\nu(C{\equiv}N)$—$\nu(C{\equiv}O)$ region of the IR spectrum of $[Mn(CO)(CNCH_3)_5][B(C_6H_5)_4]$ (as KBr pellet) appeared upon replacement of ^{12}CO by ^{13}CO; at 1900 cm^{-1} (a shift from 1949 cm^{-1}). The $Mn_2(^{13}CO)(^{12}CO)_9$ employed in this experiment was prepared by photolysis of $Mn_2(CO)_{10}$ in THF under ^{13}CO.

Because of the complexity of this reaction, little can be said about its mechanism. Ligand scrambling and oxidation-reduction appear to dominate, however.

Conclusions

Our study on photochemically induced reactions of $Mn_2(CO)_{10}$ with a number of halogen (X)-containing and metal—metal bonded compounds has furnished the following results.

Photoreactions of $Mn_2(CO)_{10}$ with the halogen-containing compounds, I_2, CH_3I, SnI_4, $CuCl_2 \cdot 2\,H_2O$, HgX_2 (X = Cl, Br or I), C_6H_5HgI and η^5-$C_5H_5Cr(NO)_2Cl$, are best rationalized in terms of the initial formation of $Mn(CO)_5^{\cdot}$ and abstraction of halogen by this radical to form $Mn(CO)_5X$. The quantum yields for the disappearance of $Mn_2(CO)_{10}$ indicate this to be generally a very efficient process. Following the abstraction, the remaining metal-containing species (usually a radical), i.e., $SnI_3^{\cdot}$, CuCl, $HgX^{\cdot}$, $C_6H_5Hg^{\cdot}$ or η^5-$C_5H_5Cr(NO)_2^{\cdot}$, undergoes (a) further abstraction of halogen by $Mn(CO)_5^{\cdot}$, (b) coupling with the $Mn(CO)_5^{\cdot}$ or (c) ligand substitution.

Photolysis of $Mn_2(CO)_{10}$ in the presence of the metal—metal bonded compounds, $(\eta^5$-$C_5H_5)_2Cr_2(NO)_4$ and $[Co_2(CNCH_3)_{10}](BF_4)_4$, does not give the respective heterodinuclear combinations, $(\eta^5$-$C_5H_5)(NO)_2CrMn(CO)_5$ and $[(CH_3NC)_5CoMn(CO)_5]^{2+}$, as detectable or isolable species. Since there is evidence that the radicals η^5-$C_5H_5Cr(NO)_2^{\cdot}$ and $[Co(CNCH_3)^{\cdot}_5]^{2+}$ are present under the conditions employed in this work, the two heterodinuclear species may possess low kinetic stability during the reaction.

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