

THE PREPARATIONS AND DECOMPOSITIONS OF SOME CHLOROACETYL-TRANSITION METAL DERIVATIVES

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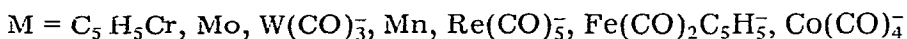
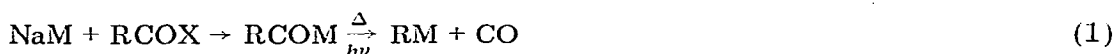
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Summary

The reactions of ClCH_2COCl with $\text{NaM}(\text{CO})_3\text{C}_5\text{H}_5$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), $\text{NaM}'(\text{CO})_5$ ($\text{M}' = \text{Mn}, \text{Re}$), $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$, $(\text{Ph}_3\text{P})_4\text{Pt}$ and $\text{Cl}(\text{CO})(\text{Ph}_3\text{P})_2\text{Ir}$ were examined. The chloroacetylmethyl derivatives, $\text{C}_5\text{H}_5(\text{CO})_3\text{MCOCH}_2\text{Cl}$ ($\text{M} = \text{Mo}, \text{W}$), $\text{C}_5\text{H}_5(\text{CO})_2\text{FeCOCH}_2\text{Cl}$, and $(\text{CO})_5\text{MnCOCH}_2\text{Cl}$, were isolated and their thermal and photochemical decompositions studied. The last complex decomposes to produce $\text{Mn}(\text{CO})_5\text{Cl}$, CO , and CH_4 , whereas the others yield the corresponding metal chlorides and ketene via β -chloride elimination. The Pt and Ir chloroacetyl complexes probably form and decompose under the reaction conditions to give the metal chloride complexes as the only isolable products.

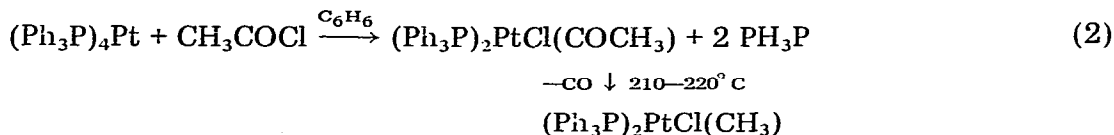
Introduction

A number of acyl and perfluoroacyl derivatives of transition metals have been prepared and successfully used for the synthesis of alkyl-, aryl- or perfluoroalkyl-transition metal species (eq. 1) [1–8].



In addition, some acyl derivatives of transition metals have also been obtained by oxidative addition of active acyl, aryl or perfluoroalkyl halides to coordinatively unsaturated transition metal species [9,10]. For example, $(\text{Ph}_3\text{P})_4\text{Pt}$ in C_6H_6 adds CH_3COCl and $\text{C}_6\text{H}_5\text{COCl}$. Also, $\text{Cl}(\text{CO})(\text{Ph}_3\text{P})_2\text{M}$ ($\text{M} = \text{Rh}, \text{Ir}$) readily adds active acyl halides [11,12]. Some of these oxidative addition products have been decarbonylated thermally or photochemically to give alkyl or aryl derivatives of transition metals.

However, no systematic investigation of the chemistry of monohaloacyl-metal complexes except for fluoro derivatives has been done. The importance



of such an investigation stems from the fact that α -monohaloacylmetal species are expected to produce α -monohaloalkylmetal derivatives via thermal or photochemical decarbonylation. The monohaloalkyl-transition metal complexes might then be used as precursors of electrophilic metal carbenes via their interactions with Lewis acids [14–18]. Such carbene complexes are believed to be the active species in the olefin metathesis reaction. From this point of view, the development of a general synthetic route for α -monohaloalkylmetal complexes is quite important.

As a result, we examined the reactions of ClCH_2COCl with a variety of transition metal derivatives and investigated the thermal and photochemical decompositions of the resulting metal acyl complexes. This paper is a description of that work.

Experimental

All experimental manipulations were routinely performed under N_2 . Solvents were deaerated with nitrogen and dried over molecular sieves. A freshly distilled, dry THF was used whenever required. Infrared spectra were obtained on either Beckman IR-4240 or Perkin–Elmer grating infrared spectrophotometers. Values are given in cm^{-1} units. NMR spectra were obtained on a Varian T-60 spectrometer. Values are given in δ (ppm) downfield from TMS ($\delta = 0$). Mass spectra were obtained on an AEI MS 902 mass spectrometer with direct inlet system. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Preparation of $\text{ClCH}_2\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$

A solution of $\text{NaMo}(\text{CO})_3\text{C}_5\text{H}_5$ was made by the usual procedure [7] from a mixture of 3.0 g of $(\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3)_2$, excess 1% sodium amalgam and 100 ml of THF. The resulting $\text{NaMo}(\text{CO})_3\text{C}_5\text{H}_5$ solution was cooled to -78°C and treated dropwise with 1.0 ml of ClCH_2COCl in 5 ml of THF. The reaction mixture was stirred at 0°C for 2 h, whereupon the solvent was removed under reduced pressure, and the resulting residue was washed with 50 ml of n-pentane, then extracted with 90 ml of CH_2Cl_2 in three portions. The resulting solution was filtered and concentrated. Addition of n-hexane followed by storage of the solution overnight in a deep freeze, afforded 2.7 g of orange crystals (69% yield), m.p. $82\text{--}84^\circ\text{C}$. Anal.: Found: C, 37.12; H, 2.27. Calcd. for $\text{C}_{10}\text{H}_7\text{ClMoO}_4$: C, 37.24; H, 2.19%. For IR and NMR, see Table 1.

Preparation of $\text{ClCH}_2\text{COW}(\text{CO})_3\text{C}_5\text{H}_5$

A solution of $\text{NaW}(\text{CO})_3\text{C}_5\text{H}_5$ was prepared by refluxing $\text{W}(\text{CO})_6$ (3.0 g) with a 20% excess of NaC_5H_5 solution in 70 ml of THF/dimethoxyethane [7]. $\text{ClCH}_2\text{COW}(\text{CO})_3\text{C}_5\text{H}_5$ was then prepared in a manner similar to $\text{ClCH}_2\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$ from 0.7 ml of ClCH_2COCl . Orange crystals (2.1 g) were obtained

TABLE 1
METAL CHLOROACETYL DERIVATIVES

Compound	Metal—CO bands ^a (cm ⁻¹)	Acyl—CO bands ^a (cm ⁻¹)	NMR δ (ppm) from TMS
ClCH ₂ COMo(CO) ₃ C ₅ H ₅	2020s, 1954s, 1935s, 1927s	1648s	3.59 (CH ₂) ^b 4.01 (Cp)
ClCH ₂ COW(CO) ₃ C ₅ H ₅	2003s, 1952s, 1932—1907vs (br)	1642s	3.73 (CH ₂) ^b 4.17 (Cp)
ClCH ₂ COMn(CO) ₅	2110m, 2000—1980vs, 1955s	1652s	4.37 (CH ₂) ^c

^a KBr pellets. ^b In C₆H₆. ^c Acetone-*d*₆.

(yield 60%), m.p. 109—111°C. Anal.: Found: C, 29.65; H, 1.82. Calcd. for C₁₀H₇ClO₄W: C, 29.26; H, 1.71%. For IR and NMR, see Table 1.

Preparation of ClCH₂COMn(CO)₅

A solution of NaMn(CO)₅ was made by vigorously stirring a mixture of 2.0 g of Mn₂(CO)₁₀, excess 1% sodium amalgam and 70 ml of THF according to the usual procedure. The NaMn(CO)₅ solution was cooled to -78°C and treated dropwise with 0.8 ml of ClCH₂COCl in 5 ml of THF, then stirred at 0°C for 10 h. Subsequently, the solvent was removed under reduced pressure and the intense yellow residue was extracted with 25 ml of CH₂Cl₂ and filtered. Addition of n-hexane to the filtrate gave 1.5 g of bright yellow crystals of ClCH₂COMn(CO)₅ (54% yield), m.p. 82—84°C (dec.). Anal.: Found: C, 30.27; H, 0.78; Cl, 13.19. Calcd. for C₇H₂ClMnO₆: C, 30.86; H, 0.74, Cl, 13.01%. For IR and NMR, see Table 1. This compound has been prepared previously in 36% yield [19].

Attempted preparation of ClCH₂CORe(CO)₅

The reaction between NaRe(CO)₅ and ClCH₂COCl gave a faint yellow powder, with a trace amount of some acetyl complex (1650 cm⁻¹). Elemental analysis gave C, 21.48; H, trace; Cl, 6.59. The results of the analysis do not correspond either to the values calculated for Re(CO)₅Cl (C, 16.60; Cl, 9.80) nor to those of the desired product, ClCH₂CORe(CO)₅ (C, 21.68, H, 0.52; Cl, 9.14).

Reaction of NaFe(CO)₂C₅H₅ with ClCH₂COCl

The reaction between NaFe(CO)₂C₅H₅ [7] and ClCH₂COCl gave mostly the dimer, [C₅H₅Fe(CO)₂]₂. Extraction of the crude product with petroleum ether, followed by chromatography over Florisil allowed the isolation of an orange-red powder with low frequency ν (CO) bands at 1645 and 1757 cm⁻¹, the latter being due to traces of [C₅H₅Fe(CO)]₂ which could not be removed by recrystallization. The mixture was then sublimed at 80°C/0.01 Torr to give 0.2 g (11%) of CH₃COFe(CO)₂C₅H₅ as a yellow-orange sublimate, m.p. 53—56°C (lit. [9]: 56—57°C). The NMR spectrum (C₆D₆ soln.) exhibited resonances at δ 2.03 (CH₃) and δ 3.77 (Cp) with relative intensities 3 : 5 (lit. [9]: δ 2.57 and δ 4.87 (CDCl₃ soln.)). Anal.: Found: C, 49.56; H, 3.98. Calcd.: C, 49.13; H, 3.67%.

Reaction of $(\text{Ph}_3\text{P})_4\text{Pt}$ with ClCH_2COCl

This reaction quantitatively gave *cis*- $(\text{Ph}_3\text{P})\text{PtCl}_2$. However, the IR spectrum of the crude product (KBr pellets) exhibit weak bands at 1635 cm^{-1} and 1675 cm^{-1} , probably due to the presence of trace amounts of metal acetyl complexes.

Similar to this reaction was the quantitative formation of $\text{Cl}_3(\text{CO})(\text{Ph}_3\text{P})_2\text{Ir}$ when $\text{Cl}(\text{CO})(\text{Ph}_3\text{P})_2\text{Ir}$ was treated with ClCH_2COCl in C_6H_6 . The IR spectrum of the crude product showed a weak absorption band at 1625 cm^{-1} , again probably due to the desired acetyl metal complex.

Thermal decomposition of $\text{ClCH}_2\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$

In a 50 ml Schlenk flask, connected to a liquid-nitrogen-cooled gas trap, was placed 0.395 g of $\text{ClCH}_2\text{COMo}(\text{CO})_3\text{Cp}$. The system was evacuated and the sample portion heated to 75°C for 1 h. The condensed pyrolysis product (products) was analyzed with infrared and mass spectroscopy, and identified as ketene [20] with traces of diketene [21].

Weight before heating, 0.3950 g; weight after heating, 0.3356 g; % wt. loss, 15.03; calcd. % wt. loss (assuming CH_2CO was lost), 13.03. IR (gas): 3260w , 3076w , 2151m , 1918w^* , 1717w^* , 1400m , 1372m , 1133m , 1108m , 890w^* , 804w^* , 875w^* (lit. [20,21]). The mass spectrum exhibited peaks corresponding to $\text{C}_4\text{H}_4\text{O}_2^+$ (m/e 84) and $\text{C}_2\text{H}_2\text{O}^+$ (m/e 42).

The residue from this decomposition reaction was identified as $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$, m.p. $140\text{--}145^\circ\text{C}$ (variable, dec.) (lit. [22]: 145°C (dec.)). IR (CCl_4 soln.; $\nu(\text{CO})$): 2052s , 1978s , 1956s (lit. [23]: 2055vs , 1980vs , 1960vs).

Photochemical decomposition of $\text{ClCH}_2\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$

$\text{ClCH}_2\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$ (0.5 g) was dissolved in 300 ml of petroleum ether (b.p. $30\text{--}40^\circ\text{C}$) and photolyzed for 1 h, whereupon the mixture was filtered to give an orange solution and a grey precipitate. The grey residue appeared to be the major product of the photolysis.

The precipitate was extracted with CH_2Cl_2 , filtered and concentrated. Addition of *n*-hexane gave an orange precipitate, identified as $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$ (see above).

The residue from the filtrate was largely $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$, however, in addition to the NMR peak corresponding to $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$, there were two weak but sharp resonances at $3.94\ \delta$ and $3.50\ \delta$ with relative intensities 5 : 2. This probably was due to the presence of trace amounts of $\text{ClCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$.

Thermal decomposition of $\text{ClCH}_2\text{COW}(\text{CO})_3\text{C}_5\text{H}_5$

$\text{ClCH}_2\text{COW}(\text{CO})_3\text{C}_5\text{H}_5$ was heated at 85°C for 45 min in a manner similar to that described for $\text{ClCH}_2\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$. Weight before heating, 0.6000 g; weight after heating, 0.5230 g; % wt. loss, 12.28; calculated. % wt. loss (assuming CH_2CO was lost), 10.24.

Two gaseous products, one condensable at -196°C , and the other not condensable at -196°C , were obtained. The latter's infrared spectrum exhibited

* Peaks due to diketene.

absorption bands at 2140w (free CO) and at 1300vw (probably due to CH₄). The infrared and mass spectra of the former gas identified it as largely ketene with traces of diketene (see above).

The residue from the pyrolysis reaction was identified as C₅H₅W(CO)₃Cl, m.p. 157–160°C (dec.) (lit. [24]: 160°C (dec.), NMR (C₆D₆ soln.) δ 4.0 (cp); IR (CCl₄ soln.; ν(CO)) 2045s, 1964vs, 1916s (lit. [25]: 2049, 1969, 1919).

Photochemical decomposition of ClCH₂COW(CO)₃C₅H₅

ClCH₂COW(CO)₃C₅H₅ (0.9 g) was photolyzed in a manner similar to that described for ClCH₂COMo(CO)₃C₅H₅ for a period of 2 h. However, only C₅H₅-W(CO)₃Cl was isolated from the reaction mixture (see above).

Thermal decomposition of ClCH₂COMn(CO)₅

ClCH₂COMn(CO)₅ (0.5325 g) was thermally decomposed in a manner similar to that for ClCH₂COW(CO)₃C₅H₅ at 70°C for 1 h. Only CO and CH₄ were identified as the gaseous products (IR and mass spectrum). The residue was washed with petroleum ether (b.p. 30–60°C), and sublimed at 45°C/0.1 Torr. A yellow sublimate, Mn(CO)₅Cl and an orange residue, (Mn(CO)₄Cl)₂ were obtained. Mn(CO)₅Cl: IR (CHCl₃; ν(CO)) 2057s, 2001s (lit. [23]: 2138w, 2054 s, 1999m). (Mn(CO)₅Cl)₂: IR (CHCl₃; ν(CO)) 2055s, 2018s, 1976s, 1957s (lit. [26]: 2061, 2023, 1982, 1952). Weight before heating, 0.5325 g; weight after heating, 0.4233 g; % wt. loss, 20.5; calcd. % wt. loss (assuming Mn(CO)₅Cl was formed), 18.2.

Photochemical decomposition of ClCH₂COMn(CO)₅

ClCH₂COMn(CO)₅ (1.1 g) was photolyzed for 1 h in the manner described above. However, only Mn(CO)₅Cl was obtained. Nevertheless, the residue from the filtrate exhibit an NMR resonance at 5.3 δ. This was clearly different from that of ClCH₂COMn(CO)₅ (4.37 δ). The new resonance was probably due to a trace amount of ClCH₂Mn(CO)₅, which could not be separated from the larger amount of ClMn(CO)₅.

Discussion

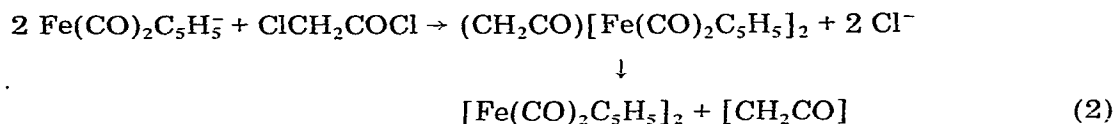
Although the chloroacetylmethyl derivatives apparently have been obtained in trace quantities in many of the attempted preparations, we were able to obtain only ClCH₂COM (M = Mo(CO)₃C₅H₅, W(CO)₃C₅H₅, Mn(CO)₅) in fairly good yields. The manganese derivative has been previously reported and the physical properties reported are in reasonable agreement with those obtained here. The NMR and IR (M–CO and acyl–CO) values of these complexes are summarized in Table 1.

The molybdenum and tungsten complexes are orange in color and the manganese derivative is bright yellow. All are heat sensitive and photosensitive. These chloroacetylmethyl complexes are readily soluble in C₆H₆, CH₂Cl₂ and CHCl₃, but sparingly soluble in n-pentane or n-hexane.

The failure to prepare ClCH₂COCr(CO)₃C₅H₅ was not surprising, since previous investigators were also unable to make RCOCr(CO)₃C₅H₅ and RfCOCr(CO)₃C₅H₅ (R = alkyl or aryl; Rf = perfluoroalkyl) [7]. The failure to obtain

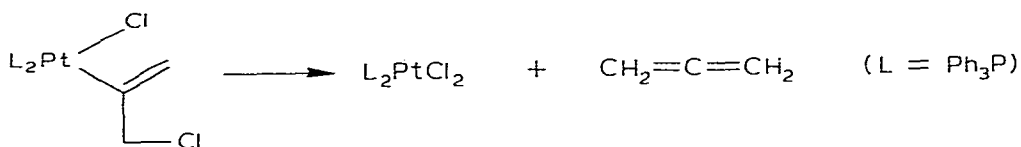
the rhenium derivative may be due to the difficulty of making pure $\text{NaRe}(\text{CO})_5$ from $\text{Re}_2(\text{CO})_{10}$ and sodium amalgam.

The quantitative formation of the dimer, $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$, in the reaction between $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and ClCH_2COCl suggests that the iron anion is so reactive [27] (and least selective) that the chlorines at both ends of the chloroacetyl chloride are replaced. The resulting product is expected to be unstable and subsequently to decompose to the dimer.



This reaction apparently is similar to the reaction between $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and 1,2-dibromoethane [8]. While compounds of the general formula $(\text{CH}_2)_n\text{[Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$ ($n = 3, 4, 5, 6$) have been successfully made, efforts to make $(\text{CH}_2)_2\text{[Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$ always lead to the quantitative formation of the dimer [8]. The formation of $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ is also rather perplexing. In an attempt to separate any minor products from the major product (the iron dimer), we resorted to chromatography of petroleum ether extracts. It may be that some $\text{C}_5\text{H}_5(\text{CO})_2\text{FeCH}_2\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ was present and was protonated by surface hydroxyl groups on the Florisil, giving the observed acetyliron complex.

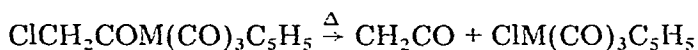
In reactions involving ClCH_2COCl and $(\text{Ph}_3\text{P})_4\text{Pt}$ or $\text{Cl}(\text{CO})(\text{Ph}_3\text{P})_2\text{Ir}$, it appeared that oxidative addition of the chloroacetyl chloride did take place, but the resulting derivatives were unstable under the experimental conditions and decomposed spontaneously to give the metal halide species via β -elimination of chloride. β -Elimination of chloride has been observed once previously from the 1-chloro-2-propenyl complex, I, to give L_2PtCl_2 and allene [28].



(I)

Various Σ -chloroethyl derivatives of transition metals have also been observed to form the corresponding ethylene and the metal chloride via β -chloroelimination [29–32].

The formation of ketene and diketene in the thermal decomposition of $\text{ClCH}_2\text{COM}(\text{CO})_3\text{C}_5\text{H}_5$ ($\text{M} = \text{Mo}, \text{W}$) also suggests that β -chloride elimination is an extremely facile process. The diketene was thought to arise from the ketene which is known to dimerize rather readily.

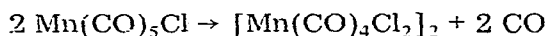


$\text{M} = \text{Mo}, \text{W}$

The mass spectrum of $\text{ClCH}_2\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$ exhibited peaks corresponding

to the parent ion (m/e 322) and $\text{ClMo}(\text{CO})_3\text{C}_5\text{H}_5^+$ (m/e 282). The absence of a peak corresponding to $\text{ClCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5^+$ (m/e 294) was a clear indication of the absence of the decarbonylation reaction in the mass spectrometer. On the other hand, the formation of CO^+ and the presence of a peak corresponding to $\text{ClCH}_2\text{W}(\text{CO})_3\text{C}_5\text{H}_5$ (m/e 382) in the mass spectrum of the tungsten complex, $\text{ClCH}_2\text{COW}(\text{CO})_3\text{C}_5\text{H}_5$ clearly showed that in the tungsten complex, both β -chlorine elimination and decarbonylation take place simultaneously in the mass spectrometer. The thermal decomposition of the tungsten complex also gave small quantities of CO and CH_4 in addition to ketene, the major gaseous product. The presence of CH_4 in the gaseous products is evidence for the intermediacy of a carbene complex in the thermal decomposition of the chloroacetyltungsten derivative [33].

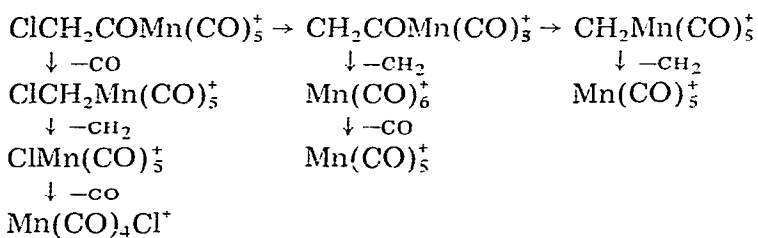
The thermal decomposition of $\text{ClCH}_2\text{COMn}(\text{CO})_5$ appeared to be different from the decomposition of $\text{ClCH}_2\text{COM}(\text{CO})_3\text{C}_5\text{H}_5$ ($M = \text{Mo}, \text{W}$). No ketene or diketene was obtained. Instead, CO and CH_4 were obtained. Again, the observation of CO and CH_4 implies the intermediacy of manganese carbene complexes in the thermal decomposition of $\text{ClCH}_2\text{COMn}(\text{CO})_5$. The $[\text{Mn}(\text{CO})_4\text{Cl}]_2$ undoubtedly arises from the thermal dimerization of $\text{ClMn}(\text{CO})_5$.



The mass spectral fragmentation pattern of $\text{ClCH}_2\text{COMn}(\text{CO})_5$ (Scheme I) also supports the thermal results in that fragments due to the methylene complex ion, $\text{CH}_2\text{Mn}(\text{CO})_5^+$, are seen. Corresponding fragments are absent in the mass spectrum of $\text{CpMo}(\text{CO})_3\text{COCH}_2\text{Cl}$ which gives only ketene and diketene upon thermal decomposition.

SCHEME I.

Proposed fragmentation pattern of $\text{ClCH}_2\text{COMn}(\text{CO})_5^+$.



The photochemical decompositions of the chloroacetylmethyl derivatives ($\text{ClCH}_2\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$, $\text{ClCH}_2\text{COW}(\text{CO})_3\text{C}_5\text{H}_5$, $\text{ClCH}_2\text{COMn}(\text{CO})_5$) produced the metal halides, $\text{ClMo}(\text{CO})_3\text{C}_5\text{H}_5$, $\text{ClW}(\text{CO})_3\text{C}_5\text{H}_5$ and $\text{ClMn}(\text{CO})_5$, respectively. The data gathered were not sufficient to tell if the metal halides were produced by β -halogen eliminations or by decarbonylation followed by the decomposition of the resulting chloromethylmetal derivatives which are known to be highly photosensitive, decomposing to produce the corresponding metal halides. In order to determine if β -halogen elimination or decarbonylation is involved, the gaseous products of these reactions must also be analyzed.

Conclusion

We have been able to synthesize ClCH_2COM ($\text{M} = \text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$, $\text{W}(\text{CO})_3\text{-C}_5\text{H}_5$, and $\text{ClCH}_2\text{COMn}(\text{CO})_5$) in fairly good yields. The thermal decompositions of $\text{ClCH}_2\text{COMo}(\text{CO})_3\text{C}_5\text{H}_5$ and $\text{ClCH}_2\text{COW}(\text{CO})_3\text{C}_5\text{H}_5$ produced the metal halide and ketene via β -halogen eliminations. $\text{ClCH}_2\text{COMn}(\text{CO})_5$ appeared to decarbonylate followed by the decomposition of the resulting chloromethyl-manganese complex to $\text{ClMn}(\text{CO})_5$. The photochemical decompositions of these metal chloroacyl derivatives quantitatively gave the metal halides.

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