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A NOVEL SYNTHESIS OF CARBENE COMPLEXES OF MANGANESE AND MOLYBDENUM CONTAINING THE TRICHLOROGERMYL GROUP

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SUMMARY

A number of carbene complexes of formulas $Cl_3GeMn(CO)_4C(OR')R$ and $C_5H_5Mo(CO)_2(GeCl_3)C(OR')CH_3$ ($R = CH_3$, C_6H_5; $R' = CH_3$, C_2H_5) have been prepared by the reaction of $[N(C_2H_5)_4]GeCl_3$ with $CH_3Mn(CO)_5$, $C_6H_5Mn(CO)_5$, or $C_5H_5Mo(CO)_3CH_3$ followed by alkylation of the resulting trichlorogermylacylcarbonylmetallate ion. The compound $C_5H_5Mo(CO)_2(GeCl_3)$-$\overline{COCH_2CH_2C}H_2$ has been prepared directly by the reaction of $[N(C_2H_5)_4]GeCl_3$ with $C_5H_5Mo(CO)_3(CH_2)_3Br$.

INTRODUCTION

In accordance with our recent interest in the sometimes unusual properties of transition-metal carbene complexes containing Group IVB ligands,[1,2] we have recently undertaken the preparation of trichlorogermyl metal-carbene complexes. We report here the synthesis of carbene complexes of manganese and molybdenum containing the trichlorogermyl group.

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In order to prepare these compounds, a seldom exploited but potentially powerful reaction scheme was used, in which an anionic nucleophile is reacted with an alkyl-metal carbonyl complex to yield an acylcarbonylmetallate ion. This is, of course, a special case of the well-known nucleophile-promoted carbonylation reaction in metal-alkyl complexes. The resulting acylcarbonylmetallate ion is then alkylated at the oxygen atom of the acyl group to yield the desired carbene complex.

Some precedents exist for this sort of reaction. First, the complex $Mn_2(CO)_9C(OCH_3)CH_3$ has been prepared by the reaction of $CH_3Mn(CO)_5$ with $Mn(CO)_5^-$ followed by methylation with $(CH_3)_3OBF_4$.[3] Also, a number of alkyl-metal carbonyl complexes have been reacted with cyanide ion to yield acyl(cyano) carbonylmetallate ions;[4] although these ions undergo only N-alkylation to give acyl (carbonyl) metal isocyanide complexes,[5] the cyclic carbene complex $C_5H_5Mo(CO)_2(CN)\overline{COCH_2CH_2CH_2}$ has been prepared by the reaction of $C_5H_5Mo(CO)_3(CH_2)_3Br$ with cyanide ion. Presumably this reaction proceeds *via* an analogous acyl-metal anion, in which the acyl ligand cyclizes with loss of bromide ion to give the observed product.[5] Finally, stable hydroxycarbene complexes $Mn(CO)_4(X)C(OH)CH_3$ (X = Br, I) have been prepared by the reaction of halide ions with $CH_3Mn(CO)_5$ followed by protonation.[6]

This sort of reaction scheme seemed ideally suited to the preparation of trichlorogermyl-metal carbene complexes. Salts of the $GeCl_3^-$ anion are well known and easily prepared, and the anion is known to exhibit nucleophilic properties.[7] Moreover, it was anticipated that the acyl(trichlorogermyl)-carbonylmetallate ion intermediates would not be accessible by the more usual route of reacting trichlorogermyl metal carbonyls with organolithium or Grignard reagents, due to the expected tendency for these reagents to attack the trichlorogermyl group rather than a carbonyl ligand.

RESULTS AND DISCUSSION

Analytical, infrared and NMR data on all compounds are presented in Tables I, II, and III.

The compound $[N(C_2H_5)_4]GeCl_3$ reacted with $CH_3Mn(CO)_5$, $C_6H_5Mn(CO)_5$, and $C_5H_5Mo(CO)_3CH_3$, to produce the salts $[N(C_2H_5)_4][Cl_3GeMn(CO)_4C(O)CH_3]$, $[N(C_2H_5)_4][Cl_3GeMn(CO)_4C(O)C_6H_5]$ and $[N(C_2H_5)_4][C_5H_5Mo(CO)_2(GeCl_3)C(O)CH_3]$, respectively, in good yield. These ionic compounds could be isolated, and would react further with trialkyloxonium salts to yield the desired carbene complexes:

$$\begin{tikzcd}
{[N(C_2H_5)_4]GeCl_3 + RMn(CO)_5} \arrow[r] & {[N(C_2H_5)_4][Cl_3GeMn(CO)_4C(O)R]\ (Ia)} \arrow[d, "R'_3O^+"] \\
& {Cl_3GeMn(CO)_4C(OR')R\ (Ib)}
\end{tikzcd}$$

$$\begin{tikzcd}
{[N(C_2H_5)_4]GeCl_3 + C_5H_5Mo(CO)_3CH_3} \arrow[r] & {[N(C_2H_5)_4][C_5H_5Mo(CO)_2(GeCl_3)\text{-}C(O)CH_3]\ (IIa)} \arrow[d, "R'_3O^+"] \\
& {C_5H_5Mo(CO)_2(GeCl_3)C(OR')CH_3\ (IIb)}
\end{tikzcd}$$

$$(R = CH_3,\ C_6H_5;\ R' = CH_3,\ C_2H_5)$$

All these compounds were characterized by analysis and by the usual spectroscopic techniques. Their structures

TABLE I

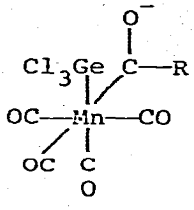
ANALYTICAL DATA[a]

Compound	M.P.	Analysis[b]	Calcd.	(Found)	
	(°C)	%C	%H	%N	%Cl
$[N(C_2H_5)_4][Cl_3GeMn(CO)_4C(O)CH_3]$	130-131	32.4 (32.3)	4.4 (4.5)	2.7 (2.7)	20.5 (20.9)
$Cl_3GeMn(CO)_4C(OCH_3)CH_3$	67- 68	20.8 (21.2)	1.5 (1.5)	. . .	26.4 (24.8)
$Cl_3GeMn(CO)_4C(OC_2H_5)CH_3$	68- 69	23.0 (23.2)	1.9 (2.0)	. . .	25.5 (26.0)
$[N(C_2H_5)_4][Cl_3GeMn(CO)_4C(O)C_6H_5]$	(oil)	39.2 (38.9)	4.3 (4.5)	2.4 (2.4)	18.3 (19.0)
$Cl_3GeMn(CO)_4C(OCH_3)C_6H_5$	162-165	30.9 (30.6)	1.7 (1.8)	. . .	22.9 (22.7)
$Cl_3GeMn(CO)_4C(OC_2H_5)C_6H_5$	103-104	32.5 (32.5)	2.1 (2.1)	. . .	22.2 (18.0)
$[N(C_2H_5)_4][C_5H_5Mo(CO)_2$ - $(GeCl_3)C(O)CH_3]$	85- 86	35.9 (35.9)	4.9 (5.0)	2.5 (2.6)	18.7 (18.9)
$C_5H_5Mo(CO)_2(GeCl_3)C(OCH_3)CH_3$	150-151	26.4 (26.7)	2.4 (2.3)	. . .	23.5 (23.1)
$C_5H_5Mo(CO)_2(GeCl_3)C(OC_2H_5)CH_3$	165-167	28.2 (28.4)	2.8 (3.0)	. . .	22.8 (22.9)
$C_5H_5Mo(CO)_2(GeCl_3)\overline{COCH_2CH_2CH_2}$	202-204	28.3 (28.0)	2.4 (2.5)	. . .	22.8 (23.2)

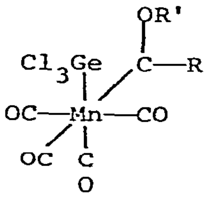
[a] Correct parent peaks were observed in the mass spectrum of all nonionic compounds

[b] Average of at least two determinations

were established by infrared spectroscopy as follows: the manganese compounds all show four peaks in the carbonyl stretching region of the infrared spectrum, characteristic of a *cis*-disubstituted octahedral complex. Accordingly these compounds are assigned the structures shown below:



Ia



Ib

TABLE II

INFRARED DATA

Compound	$\nu_{C\equiv O}$ cm^{-1}
$[N(C_2H_5)_4][Cl_3GeMn(CO)_4C(O)CH_3]$[a]	2058 s, 1981 s, 1960 vs, 1943 s
$Cl_3GeMn(CO)_4C(OCH_3)CH_3$[b]	2090 s, 2028 s, 2008 vs, 1999 s
$Cl_3GeMn(CO)_4C(OC_2H_5)CH_3$[b]	2090 s, 2030 s, 2010 vs, 2002 s
$[N(C_2H_5)_4][Cl_3GeMn(CO)_4C(O)C_6H_5]$[a]	2065 s, 1988 s, 1968 vs, 1945 s
$Cl_3GeMn(CO)_4C(OCH_3)C_6H_5$[b]	2092 s, 2030 s, 2018 vs, 2001 s
$Cl_3GeMn(CO)_4C(OC_2H_5)C_6H_5$[b]	2091 s, 2029 s, 2017 vs, 1999 s
$[N(C_2H_5)][C_5H_5Mo(CO)_2(GeCl_3)C(O)CH_3$[a]	1935 s, 1857 vs
$C_5H_5Mo(CO)_2(GeCl_3)C(OCH_3)CH_3$[b]	1987 s, 1914 vs
$C_5H_5Mo(CO)_2(GeCl_3)C(OC_2H_5)CH_3$[b]	1986 s, 1912 vs
$C_5H_5Mo(CO)_2(GeCl_3)\overline{COCH_2CH_2C}H_2$[c]	1983 s, 1911 vs

[a] acetone solution

[b] heptane solution

[c] chloroform solution

TABLE III

NMR DATA[a]

Compound	$\tau_{C-C\underline{H}_3}$[b] $(\tau_{C-C_6\underline{H}_5})$[c]	$\tau_{O-C\underline{H}_3}$[b] $(\tau_{O-C\underline{H}_2-CH_3})$[d]	$\tau_{O-CH_2-CH_3}$[e]	$\tau_{C_5H_5}$[b]
$[N(C_2H_5)_4][Cl_3GeMn(CO)_4C(O)CH_3]$[f]	7.48	...	...	...
$Cl_3GeMn(CO)_4C(OCH_3)CH_3$	6.82	5.45	...	...
$Cl_3GeMn(CO)_4C(OC_2H_5)CH_3$	6.80	(5.26)	8.24	...
$[N(C_2H_5)_4][Cl_3GeMn(CO)_4C(O)C_6H_5]$[f]	(2.65)	...	...	...
$Cl_3GeMn(CO)_4C(OCH_3)C_6H_5$	(2.65)	5.68	...	...
$Cl_3GeMn(CO)_4C(OC_2H_5)C_6H_5$	(2.65)	(5.48)	8.37	...
$[N(C_2H_5)_4][C_5H_5Mo(CO)_2(GeCl_3)C(O)CH_3]$[f]	7.58	...	...	4.87
$C_5H_5Mo(CO)_2(GeCl_3)C(OCH_3)CH_3$	6.96	5.55	...	4.40
$C_5H_5Mo(CO)_2(GeCl_3)C(OC_2H_5)CH_3$	6.93	(5.41)	8.39	4.43
	$\tau CH_2(\alpha)$[h]	$\tau CH_2(\gamma)$[i]	$\tau CH_2(\beta)$[j]	
$C_5H_5Mo(CO)_2(GeCl_3)\overline{COCH_2CH_2C}H_2$[g]	6.25	5.12	7.99	4.44

[a] $CDCl_3$ solution, except $C_5H_5Mo(CO)_2(GeCl_3)C(OC_2H_5)CH_3$, CD_2Cl_2 solution

[b] Singlet

[c] Unresolved multiplet

[d] Quartet, $J_{CH_2-CH_3} = 7.0$ Hz

[e] Triplet

[f] $N(C_2H_5)_4^+$: $\tau_{CH_2} = 6.48$ (quartet); $\tau_{CH_3} = 8.58$ (triplet); $J_{CH_2-CH_3} = 7.0$ Hz

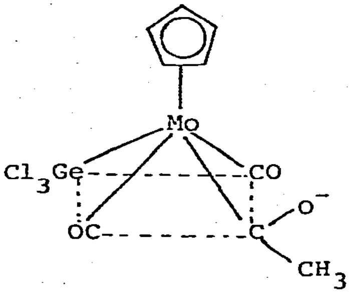
[g] 100 MHz NMR spectrum

[h] Triplet, $J_{CH_2(\alpha)-CH_2(\beta)} = 7.5$ Hz

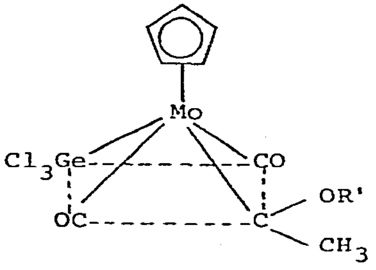
[i] Triplet, $J_{CH_2(\beta)-CH_2(\gamma)} = 7.5$ Hz

[j] Quintet

The molybdenum compounds all exhibit two carbonyl stretching peaks, as expected for either a *cis* or a *trans* geometry; in this case the geometry is determined on the basis of the relative intensities of the peaks. The fact that the lower-frequency peak (asymmetric stretch) is more intense than the higher-frequency peak (symmetric stretch) strongly indicates that the two carbonyls are *trans* to one another,[8-10] as shown below:



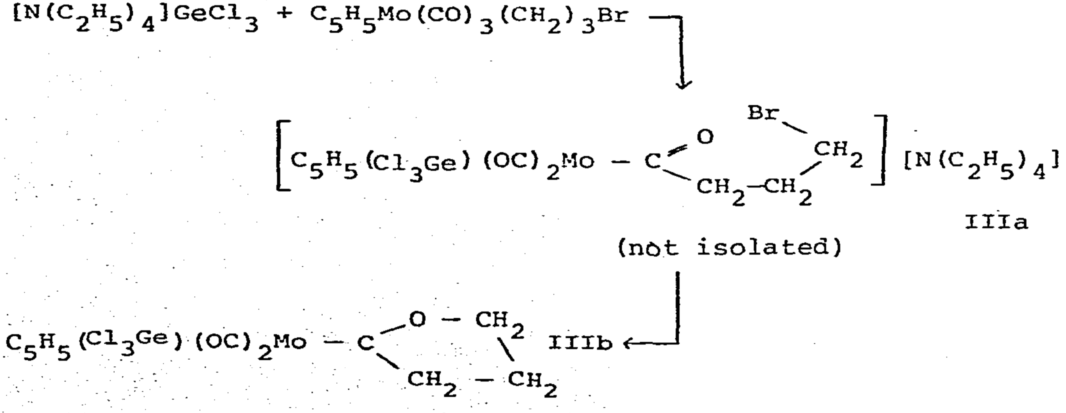
IIa



IIb

The geometries of these trichlorogermyl complexes are thus the same as those reported for other carbene derivatives of manganese and molybdenum containing the triphenylgermyl group.[1,2]

The cyclic carbene complex $C_5H_5Mo(CO)_2(GeCl_3)\overline{COCH_2CH_2CH_2}$ was prepared directly by the reaction of $[N(C_2H_5)_4]GeCl_3$ with $C_5H_5Mo(CO)_3(CH_2)_3Br$. In this case the intermediate acylcarbonylmetallate anion was not isolated:



$$[N(C_2H_5)_4]GeCl_3 + C_5H_5Mo(CO)_3(CH_2)_3Br \longrightarrow$$

$$\left[C_5H_5(Cl_3Ge)(OC)_2Mo-C(=O)CH_2-CH_2-CH_2Br\right][N(C_2H_5)_4]$$

IIIa

(not isolated)

$$\longrightarrow C_5H_5(Cl_3Ge)(OC)_2Mo-\overline{C-O-CH_2-CH_2-CH_2}$$

IIIb

This reaction proceeded much more rapidly than that between $[N(C_2H_5)_4]GeCl_3$ and $C_5H_5Mo(CO)_3CH_3$. The product was shown by infrared spectroscopy to have the same *trans* geometry as the other molybdenum complexes.

It is worth noting that no trace of any intermediate trans isomer of Ia or of any intermediate cis isomer of IIa was seen while following these reactions. In particular, the $GeCl_3^-$ - $C_5H_5Mo(CO)_2CH_3$ reaction was carefully followed (in $CHCl_3$ solution) by both infrared and nmr spectroscopy; only peaks due to the final product, the thermodynamically stable trans isomer[11] of $[C_5H_5Mo(CO)_2(GeCl_3)C(O)CH_3]^-$, were seen. Presumably in this system, unlike several others where intermediate cis acyl species are stable enough to have been observed[5,10], the rearrangement to the trans isomer occurs very rapidly.

The product isomers of the acyl anions naturally give rise to the corresponding isomers of the carbene complexes. In the case of the oxacyclopentylidene complex (IIIb), the question arises whether the cyclization occurs primarily before or after rearrangement to the trans configuration. When this reaction (in acetone) was followed in the infrared, only the peaks due to the final trans product were observed. Although he broadness of the peaks in this solvent might allow the possibility that peaks due to a cis carbene intermediate might be unresolved, it was observed that the intensity ratio of the observed peaks appeared to be characteristic of the trans isomer (vide supra) throughout the course of the reaction. It may thus be concluded that in this reaction the rearrangement to the trans acyl anion is at least substantially complete before cyclization of the ligand occurs.

It was hoped that the synthesis of the complex $[N(C_2H_5)_4][Cl_3GeMn(CO)_4C(O)CH_3]$ might provide a convenient route to a dichloro analogue of the recently-reported compounds $R_2\overline{GeMn(CO)_4C(O)}CH_3$, in which the carbene and germyl ligands appear to be connected by an oxygen bridge.[1] This route envisaged abstraction of a chloride ion by Ag^+, followed by cyclization. However, in fact the only product observed in this reaction was $Cl_3GeMn(CO)_5$, obtained in 75% yield. The mechanism by which this product is formed is not understood at present.

We believe that the synthesis of acylcarbonylmetallate ions *via* reactions of anionic nucleophiles with alkyl metal carbonyl complexes, as exemplified by the reactions reported here, may prove to be a useful route to carbene complexes. It should find particular application, as in this instance, in those cases where the desired carbene complex cannot be prepared by the more usual routes. Other possible applications of this method, as well as reactions of the resulting complexes, are under investigation.

EXPERIMENTAL

Starting materials, including $CH_3Mn(CO)_5$,[12] $C_6H_5Mn(CO)_5$,[13] $C_5H_5Mo(CO)_3CH_3$,[14] $C_5H_5Mo(CO)_3(CH_2)_3Br$,[15] and $[N(C_2H_5)_4]GeCl_3$[16] were prepared as described in the literature. Other reagents and solvents were reagent grade, and were used as obtained. All reactions were carried out under a nitrogen atmosphere.

Infrared spectra were obtained using a Perkin-Elmer Model 337 grating infrared spectrometer with scale expansion and were calibrated against gaseous CO.[17] Proton NMR data were recorded on Varian A60, 56/60, or XLFT-100 instruments. Mass spectra were taken with an AEI-MS9 mass spectrometer. Microanalyses were performed by the University of Alberta microanalytical laboratory. Melting points were determined using a Gallenkamp apparatus and are uncorrected.

Preparation of Manganese Compounds

$[N(C_2H_5)_4][Cl_3GeMn(CO)_4C(O)CH_3]$

A 1.50 g sample of $CH_3Mn(CO)_5$ (7.14 mmol) was dissolved in 50 ml. of acetone, and 2.10 g of $[N(C_2H_5)_4]GeCl_3$ (6.79 mmol) were added. The reaction was followed by monitoring the changes in the infrared spectrum and was complete after 30 min. The acetone was removed under vacuum and the yellow solid residue was freed of excess $CH_3Mn(CO)_5$ by washing with ether. The resulting crystalline product was sufficiently pure for use in further synthetic reactions; yield, 3.20 g (6.16 mmol, 91% based on $[N(C_2H_5)_4]GeCl_3$). A small quantity of recrystallized material for analysis was obtained by saturating 700 ml of ether with the compound, filtering, reducing the volume to 100 ml., and chilling the solution to -20° overnight; this yielded *ca.* 0.5 g of fine, light yellow crystals.

$[N(C_2H_5)_4][Cl_3GeMn(CO)_4C(O)C_6H_5]$ was prepared in the same manner from $[N(C_2H_5)_4]GeCl_3$ and $C_6H_5Mn(CO)_5$. This compound was obtained as an orange oil which could not be induced to crystallize. However, the oil afforded a reasonable analysis and this, in combination with the usual spectroscopic data and its subsequent chemical behavior, allowed its unambiguous characterization. Yield, 6.17 g (10.62 mmol, 92%).

$Cl_3GeMn(CO)_4C(OCH_3)CH_3$

A 1.25 g sample of $[N(C_2H_5)_4][Cl_3GeMn(CO)_4C(O)CH_3]$ (2.41 mmol) was dissolved in 50 ml. of dichloromethane and approximately a twofold excess $(CH_3)_3OPF_6$ was added. The reaction was monitored by infrared and was complete in 1 hr. The solvent was removed and the residue was extracted with ether. The extracts were filtered and the ether was removed; the residue was extracted with 200 ml of warm heptane. The filtered extracts were chilled to -20°C overnight, yielding the product as fine, off-white crystals (0.33 g, 0.82 mmol, 34%).

$Cl_3GeMn(CO)_4C(OC_2H_5)CH_3$ was prepared and worked up in the same way, using $(C_2H_5)_3OBF_4$ as the alkylating agent. Yield, 0.47 g (1.12 mmol, 58%) of off-white, needle-like crystals.

$Cl_3GeMn(CO)_4C(OCH_3)C_6H_5$ (light yellow crystals; yield, 19%) and *$Cl_3GeMn(CO)_4C(OC_2H_5)C_6H_5$* (light yellow needles; yield 31%) were also prepared similarly from $[N(C_2H_5)_4][Cl_3GeMn(CO)_4C(O)C_6H_5]$.

Preparation of Molybdenum Compounds.

$[N(C_2H_5)_4][C_5H_5Mo(CO)_2(GeCl_3)C(O)CH_3]$.

A 3.50 g portion of $C_5H_5Mo(CO)_3CH_3$ (13.5 mmol) was dissolved in 100 ml of acetone, and 3.96 g of $[N(C_2H_5)_4]GeCl_3$ (12.8 mmol) were added. The reaction was monitored by infrared and was complete after 23 hr. The solvent was removed and the product was freed of excess $C_5H_5Mo(CO)_3CH_3$ by washing with hexane. The product was then recrystallized by slow addition of ether to an acetone solution of the product; yield, 3.27 g (5.75 mmol, 44.8% based on $[N(C_2H_5)_4]GeCl_3$).

$C_5H_5Mo(CO)_2(GeCl_3)C(OCH_3)CH_3$

A 1.23 g sample of $[N(C_2H_5)_4][C_5H_5Mo(CO)_2(GeCl_3)C(O)CH_3]$ (2.16 mmol) was dissolved in 50 ml. of dichloromethane and excess $(CH_3)_3OPF_6$ was added. After 1 hr. the infrared spectrum showed that the reaction was complete. The solvent was removed, and the residue was extracted with ether. The extracts were filtered and the ether was removed; the resulting product was recrystallized from dichloromethane-heptane. Yield, 0.38 g (0.83 mmol, 38%) of yellow-green crystals.

$\underline{C_5H_5Mo(CO)_2(GeCl_3)C(OC_2H_5)CH_3}$ was prepared and worked up similarly, using $(C_2H_5)_3OBF_4$ as the alkylating agent. Yield, 0.49 g (1.05 mmol, 54%) of yellow-green crystals.

$C_5H_5Mo(CO)_2(GeCl_3)\overline{COCH_2CH_2CH_2}$

A 2.00 g sample of $C_5H_5Mo(CO)_3(CH_2)_3Br$ (5.45 mmol) was stirred in 50 ml of acetone with 1.68 g of $[N(C_2H_5)_4]GeCl_3$ (5.45 mmol). The reaction was monitored by infrared. A precipitate of $[N(C_2H_5)_4]Br$ formed quickly and the reaction was complete in 3 hr. The solution was filtered, the solvent was removed under vacuum, and the residue was recrystallized from dichloromethane by the slow addition of heptane, yielding the produc as bright yellow crystals. Yield, 0.65 g (1.39 mmol, 26%).

Reaction of $[N(C_2H_5)_4][Cl_3GeMn(CO)_4C(O)CH_3]$ *with* $AgBF_4$*:*
A 1.56 g sample of $[N(C_2H_5)_4][Cl_3GeMn(CO)_4C(O)CH_3]$ (3.01 mmol) was dissolved in 5 ml of acetone and a solution of 0.585 g of $AgBF_4$ (3.01 mmol) in 10 ml of acetone was added. A white precipitate was obtained at once, and was filtered off; this apparently consisted of AgCl as it was insoluble in water or

acetone but soluble in aqueous ammonia. The solvent was removed from the filtrate under vacuum and the residue was extracted with 50 ml of ether, and the extracts were filtered leaving a second white, acetone-soluble precipitate, apparently $[N(C_2H_5)_4]BF_4$. The filtrate was evaporated, leaving the product, which was identified as $Cl_3GeMn(CO)_5$ by its infrared[18] and mass spectra. The product was purified by sublimation at 42°/0.04 torr. Yield, 0.85 g (2.3 mmol, 75% based on Mn).

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