(2) P. Pino, *Adv. Polym. Sci.*, **4**, 393 (1965).
(3) C. S. Marvel, R. L. Frank, and E. Prill, *J. Am. Chem. Soc.*, **65**, 1647 (1943).
(4) S. Murahashi, S. Nozakura, and S. Takeuchi, *Bull. Chem. Soc. Jpn.*, **33**, 658 (1960).
(5) G. I. Fray and R. Robinson, *Tetrahedron*, **18**, 261 (1962).
(6) P. Pino, F. Ciardelli, and G. P. Lorenzi, *J. Polym. Sci., Part C*, **4**, 21 (1963).
(7) D. Braun and W. Kern, *J. Polym. Sci., Part C*, **4**, 197 (1963).
(8) F. Millich and G. K. Baker, Macromolecules, **2**, 122 (1969).
(9) (a) R. J. M. Nolte, A. J. M. van Beijnen, and W. Drenth, *J. Am. Chem. Soc.*, **96**, 5932 (1974); (b) W. Drenth and R. J. M. Nolte, *Acc. Chem. Res.*, **12**, 30 (1979).
(10) H. Yuki, K. Ohta, Y. Okamoto, and K. Hatada, *J. Polym. Sci., Polym. Lett. Ed.*, **15**, 589 (1977).
(11) K. Ohta, K. Hatada, Y. Okamoto, and H. Yuki, *J. Polym. Sci. Polym. Lett. Ed.*, **16**, 545 (1978).
(12) H. Yuki, K. Hatada, Y. Kikuchi, and T. Niinomi, *J. Polym. Sci. Part B*, **6**, 753 (1968); *Polym. J.*, **1**, 36 (1970).
(13) II was synthesized from (*R*)-N-(1-phenylethyl)aniline ($[\alpha]^{25}_{D}$ −19.4°, *c* 1g/dL, methanol) and n-BuLi in toluene: G. Wittig and U. Thiele, *Justus Liebigs Ann. Chem.*, **726**, 1 (1969).
(14) (−)-Sparteine was dried over CaH_2 and distilled; $[\alpha]^{20}_{D}$ −18.0° (*c* 4.4 g/dL, ethanol). This was mixed with *n*-BuLi in the molar ratio [sparteine]/[n-BuLi] = 1.2 in toluene at room temperature. Y. Okamoto, K. Urakawa, K. Ohta, and H. Yuki, Macromolecules, **11**, 719 (1978).
(15) To determine the tacticity and the degree of polymerization, poly(TrMA) was hydrolyzed in methanol containing a small amount of hydrochloric acid and then was converted to PMMA by methylation with diazomethane.[12]
(16) The gel permeation chromatographic analysis was accomplished on a JASCO FLC-A10 instrument with a 50 cm column of Shodex GPC-A80 using THF as eluant. Calibration curve of molecular weight was obtained from polystyrene standards. The number averaged molecular weight of the PMMA was estimated from the elution curve.

Yoshio Okamoto, Koichi Suzuki
Koji Ohta, Koichi Hatada, Heimei Yuki*
Department of Chemistry
Faculty of Engineering Science
Osaka University, Toyonaka, Osaka 560, Japan

Received April 16, 1979

Onium Ions. 19.[1] Chloromethylhalonium Ions

Sir:

In our search for nonvolatile and, therefore, safer chloromethylating agents, we report here the first preparation and study of previously unknown chloromethylhalonium ions.

When dichloromethane is dissolved in a twofold molar excess of antimony pentafluoride in sulfuryl chloride fluoride solution at −130 °C, the bis(chloromethyl)chloronium ion (**1**) is formed. The NMR parameters of **1** are given in Table I.

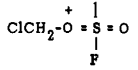
$$[ClCH_2\overset{+}{Cl}CH_2Cl]\,Sb_2F_{10}Cl^-$$

1

When sulfur dioxide is added to a solution of **1**, it forms chloromethylated sulfur dioxide **2**, whose ^1H and ^{13}C NMR shifts are δ_H 7.0 (s) and δ_C 88.8 (t), J_{C-H} = 102.1 Hz. That no chloromethylated SO_2ClF (**3**) is formed in the solution of **1** in SO_2ClF is apparent from the fact that, if **3** were the observed species, then one would expect its ^{13}C chemical shift to be ~15 ppm deshielded with respect to the ^{13}C shift of **2**, as is the case in the CH_3F-SbF_5 system in SO_2 and SO_2ClF.[2] Since the opposite trend is noted, **1** must be the observed species, in accord with the fact that CH_2Cl_2 is a better nucleophile than SO_2ClF.

$$[ClCH_2\text{-}O=\overset{+}{S}=O]\,Sb_2F_{10}Cl^-$$

2



$$ClCH_2\text{-}\overset{+}{O}=\underset{F}{\overset{Cl}{S}}=O$$

3

Table I. ^1H and ^{13}C Parameters of Chloromethylmethyl- and Bis(chloromethyl) Halonium Ions

	δ_{-CH_2-}		δ_{-CH_3}	
ion	^1H	^{13}C (J_{C-H})[b]	^1H	^{13}C (J_{C-H})
1	7.0	78.5 (194.0, t)		
4	6.8	69.0 (193.6, t)		
5	6.3	37.8 (186.8, t)		
6	6.3	80.4 (191.2, t)	4.3	50.7 (162.3, q)
7	6.2	69.4 (190.8, t)	4.1	39.3 (162.0, q)
8	6.0	38.6 (185.2, t)	3.8	12.2 (158.5, q)

[a] In parts per million from external Me_4Si capillary in SO_2ClF at −90 to −100 °C. [b] t = triplet, q = quartet. J_{C-H} in Hz.

Ions **1** and **2** are stable up to −85 °C in SbF_5-SO_2ClF solution, above which temperature they form difluoromethane.

A series of additional chloromethylhalonium ions were prepared by treating ion **1** with several monohalo- and dihaloalkanes. The ^1H and ^{13}C NMR parameters of the chloromethylhalonium ions formed are given in Table I. Halonium ions **4** and **5** were formed by treating **1** with bromochloromethane and chloroiodomethane, respectively (reaction 1). The bis(chloromethyl)iodonium ion **5** could also be prepared from $ClCH_2I$ and HF-SbF_5 in SO_2 solution at −50 °C, but attempts to prepare the related bromonium ion **4** in a similar way gave a complex mixture of products.

$$\mathbf{1} + ClCH_2X \xrightarrow[-130\,°C]{SO_2ClF} ClCH_2\overset{+}{X}CH_2Cl \qquad (1)$$

4, X = Br
5, X = I

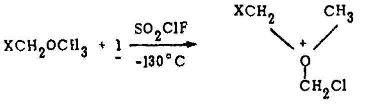
Chloromethylmethylhalonium ions **6**, **7**, and **8** were also prepared by similar methods (reaction 2). It is interesting to note that the difference between J_{CH} in bis(chloromethyl)halonium ions and the coresponding dimethylhalonium ions is uniformly 30 Hz.[3] The same trend is also observed in the chloromethylmethyl halonium ions **6**, **7**, and **8** and between **2** and $[CH_3O{=}S{=}O]^+$.

$$\mathbf{1} + CH_3X \xrightarrow[-130\,°C]{SO_2ClF} CH_3\overset{+}{X}CH_2Cl \xleftarrow[-130\,°C]{SO_2ClF} CH_3F{:}SbF_5 + ClCH_2X \qquad (2)$$

6, X = Cl
7, X = Br
8, X = I

X = Cl,Br,I

When dimethyl or chloromethylmethyl ether was added to a solution of **1**, oxonium ions **9** and **10** were formed (reaction 3). Attempts to prepare ions **9** and **10** by methylating[4] chloromethylmethyl ether or bis(chloromethyl) ether (eq 4) gave complex mixtures of ions, which did not include either **9** or **10**. Ions **11** and **12** were the major products obtained in each reaction.[5] Ion **11** was also a byproduct in reaction 3.



(3)

		δ^1H	$\delta^{13}C$	J_{CH}
9, X = H	CH_2	6.2	94.9	188.4 Hz
	CH_3	4.6	77.0	158.1
10, X = Cl	CH_2	6.5	92.7	188.0
	CH_3	4.9	76.0	159.2

$$CH_3F{:}SbF_5 + XCH_2OCH_2Y \xrightarrow[-78\,°C\text{ to }-120\,°C]{SO_2\text{ or }SO_2ClF} CH_2=\overset{+}{O}-CH_2Y \qquad (4)$$

X = Cl, Y = H
X = Y = Cl

11, Y = H
12, Y = Cl

0002-7863/79/1501-4765$01.00/0

Attempts to prepare tris(chloromethyl)oxonium ion from **1** and bis(chloromethyl) ether[6] gave only **12.** Seemingly **1** attacks preferentially the chloromethyl ethers to form **13a,b**, which then easily ionizes to **11** or **12** and CH_2Cl_2.

$$XCH_2OCH_2\overset{+}{Cl}CH_2Cl$$

13a, X = H

13b, X = Cl

The demonstration of the formation of chloromethylhalonium ions and their effective chloromethylating ability opens up the question of the possible chloromethylating ability of related precursors, including methylene chloride, which, consequently, could be of a carcinogenic nature. We are carrying out further studies relating to the in vitro chloromethylating ability of these systems.

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

References and Notes

(1) For part 18, see G. A. Olah, D. J. Donovan, H. C. Lin, H. Mayr, P. Andreozzi, and G. Klopman, *J. Org. Chem.*, **43**, 2268 (1978).

(2) G. A. Olah, D. J. Donovan, and H. C. Lin, *J. Am. Chem. Soc.*, **98**, 2661 (1976).

(3) G. A. Olah, "Halonium Ions," Wiley-Interscience, New York, 1975, and references given therein.

(4) G. A. Olah, J. R. DeMember, and R. H. Schlosberg, *J. Am. Chem. Soc.*, **91**, 2112 (1969).

(5) G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, **89**, 2993 (1967).

(6) This highly carcinogenic compound should be handled with great care: *J. Natl. Cancer Inst.*, **43**, 481 (1969). All operations involving chloromethyl ethers were carried out in an efficient "carcinogenic hood" with appropriate precautions.

George A. Olah,* Mark R. Bruce
Hydrocarbon Research Institute, Department of Chemistry
University of Southern California, University Park
Los Angeles, California 90007

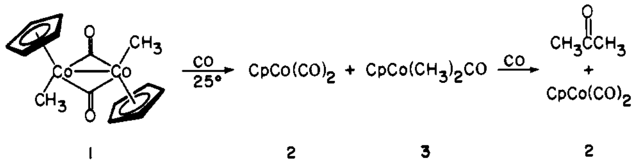
Received February 12, 1979

Reaction of a Bridged Binuclear Dialkylcobalt Complex with Carbon Monoxide and Phosphines. Observation of Competing Inter- and Intramolecular Metal to Metal Methyl Transfer

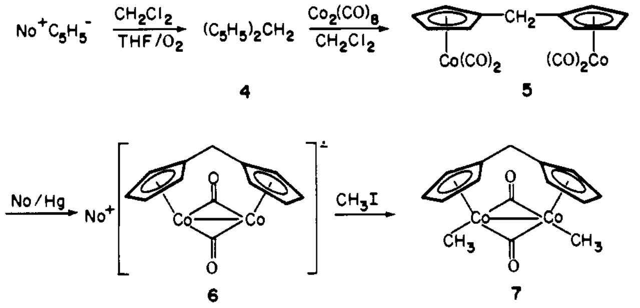
Sir:

Bis(η^5-cyclopentadienylcarbonylmethylcobalt) (**1**) reacts rapidly with carbon monoxide at ambient temperature, leading to a quantitative yield of η^5-cyclopentadienyldicarbonylcobalt (**2**) and acetone (Scheme I), a process in which a binuclear transition metal complex mediates the formation of two new carbon-carbon bonds. In a previous study,[1] we established that η^5-cyclopentadienylcarbonyldimethylcobalt (**3**) is an intermediate in this transformation. Labeling studies indicated that an intermolecular process was occurring, resulting in the formation of substantial amounts of acetone-d_3 upon carbonylation of equimolar mixtures of **1**-d_6 and **1**-d_0.

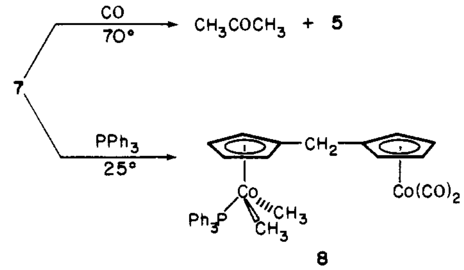
Scheme I



Scheme II



Scheme III



To determine whether this intermolecular process is on the direct pathway leading from **1** to **3**, we have now prepared **7** (Scheme II), a complex analogous to **1**, but having its two cyclopentadienyl rings joined by a methylene group. We find this structural modification allows us *to control the intramolecularity of the carbonylation reaction* by modifying reaction conditions. In addition, **7** undergoes a remarkable reaction with phosphines which sharply restricts mechanistic alternatives for these reactions.

Dicyclopentadienylmethane (**4**) was prepared[2] as a mixture of isomers and converted into the binculear tetracarbonyl **5** by the route outlined in Scheme II. As might be expected if decomposition of **1** involves initial dissociation into mononuclear fragments, complex **7** is less reactive than **1**, and requires temperatures near 70 °C to achieve carbonylation at a reasonable rate. Under these conditions, the chemistry of **7** is quite comparable with that of **1**, and acetone and tetracarbonyl complex **5** are produced in quantitative yield. Unlike **1**, however, the carbonylation can be made to follow a predominantly intra- or intermolecular pathway by varying the concentration

Table I. Isotope Labeling Data Obtained in Crossover Experiments on the Reaction of Mixtures 7-d_0 and 7-d_6 with CO and PPh_3

starting complex			entering ligand	T, °C	acetone products,[a] %			molecularity	
total concn, M	7-d_0, %	7-d_6, %			d_0	d_3	d_6	% intra-	% inter-
0.25	53	47	CO[b]	70	40	28	32	44	56
0.05	55	45	CO[b]	70	52	5	43	90	10
0.25	46	54	PPh_3[c]	25	38	16	46	67	33
0.05	49	51	PPh_3[c]	25	49	1	50	98	2
0.25	69	31	PPh_3[c]	70	69	3	28	93	7

[a] In the carbonylation reactions, where acetone was formed as direct product, it was either isotropically analyzed by GC/MS or purified by preparative GC and then subjected to subsequent MS analysis. In the PPh_3 reaction, product **8** was first diluted to a concentration $\leq$0.05 M and then carbonylated to generate acetone for analysis (the run at 0.05 M **7** precludes the possibility of significant label scrambling during the carbonylation of **8** at these concentrations). [b] Toluene solvent. [c] Benzene solvent.

0002-7863/79/1501-4766$01.00/0