Scheme I

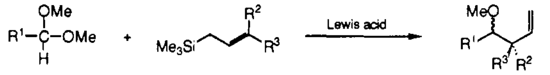


Table I. Effect of Lewis Acid in the Cyclization of **1a** → **4a**/**5a**[a]

entry	reagent	temp, °C	% syn (**4a**)[b]	% anti (**5a**)[b]	yield, %[b,c] (mass recovery)
1	Me_3SiOTf	−70	96	4	100
2	TfOH	−70	96	4	62 (74)
3	$Ti(OiPr)_2Cl_2$	−20	87	13	21 (91)
4	$AlCl_3$	−20	86	14	33 (78)
5	BCl_3	−70	82	18	57 (73)
6	$BF_3{\cdot}OEt_2$	−20	77	23	95 (100)
7	$TiCl_4$	−90	47	53	55 (58)
8	$SnCl_4$ (1.0 equiv)	−70	45	55	35 (60)
9	$SnCl_4$ (0.5 equiv)	−60	71	29	81 (81)

[a] All cyclizations were performed in CH_2Cl_2 (0.05 M) with 1.0 equiv of Lewis acid (except entry 9). At least 3 runs with each Lewis acid (±3%). [b] Ratios and yields were calculated based on independently determined response factors vs cyclododecane. [c] Yield is based on **4a** + **5a** vs cyclododecane; mass recovery is total integrated area including products of protiodesilylation.

Table II. Effect of Lewis Acid in the Cyclization of **2a** → **4a**/**5a**[a]

entry	reagent	temp, °C	% syn (**4a**)	% anti (**5a**)	yield, % (mass recovery)
1	Me_3SiOTf	−70	93	7	100
2	$BF_3{\cdot}OEt_2$	−60	94	6	63 (85)
3	$TiCl_4$	−70	41	59	44 (49)
4	$SnCl_4$	−30	38	62	25 (25)

[a] See footnotes Table I.

Table III. Effect of Acetal Structure in the Cyclization of **1** and **2** → **4**/**5** with TMSOTf[a]

substrate	ML'_3	R	% syn (**4**)[b]	% anti (**5**)[b]
1a	$SiMe_3$	Me	96	4
1b	$SiMe_3$	Et	92	8
1c	$SiMe_3$	*i*Bu	90	10
1d	$SiMe_3$	*i*Pr	38	62
2a	$SnBu_3$	Me	93	7
2b	$SnBu_3$	Et	92	8
2d	$SnBu_3$	*i*Pr	43	57

[a] All cyclizations were performed in CH_2Cl_2 (0.05 M) with 1.0 equiv of TMSOTf for **1** and 2.0 equiv for **2**. At least 3 runs with each substrate (±3%). [b] Ratios were calculated on independently determined response factors vs cyclododecane. All yields were >95%.

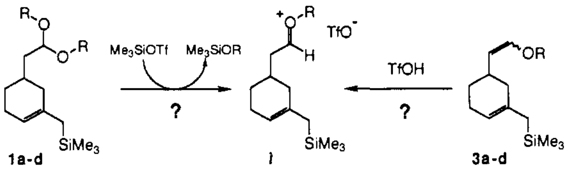
Table IV. Effect of Enol Ether Structure in the Cyclization of **3** → **4**/**5**[a]

substrate	R	*E*/*Z*[b]	temp, °C	% syn (**4**)[c]	% anti (**5**)[c]	yield, %[c]
(*E*)-**3a**	Me	96/4	−50	60	40	25[d]
(*Z*)-**3a**	Me	0/100	−70	53	47	79
(*E*)-**3b**	Et	100/0	−70	31	69	76
(*Z*)-**3b**	Et	23/77	−70	38	62	74
(*E*)-**3d**	*i*Pr	100/0	−70	25	75	84
(*Z*)-**3d**	*i*Pr	0/100	−70	27	73	76

[a] All cyclizations were performed in CH_2Cl_2 (0.05 M) with 0.95 equiv of TfOH. At least 3 runs with each substrate (±3%). [b] Established by capillary GC analysis. [c] Ratios and yields determined by independently determined response factors vs cyclododecane. [d] The major product resulted from protiodesilylation.

TMSOTf these methyl, ethyl, and probably isobutyl acetals react via an S_N2-type mechanism, while the isopropyl acetals react via prior ionization to an oxocarbenium ion (i). Accordingly, these conclusions are supported by the observed Lewis acid dependences wherein the nature of the Lewis acid acetal complex is expected to influence the S_N2-type reaction. Furthermore, the inherent strain in diisopropyl acetals should favor ready ionization compared to ethyl and methyl analogues.

Scheme II



Studies are in progress on the structure of Lewis acid acetal complexes and the stereochemical course of reactions with cyclic acetals.

Acknowledgment. We gratefully acknowledge financial support by grants from the National Science Foundation (NSF CHE 8515371). S.E.D. also acknowledges support from the NSF (Presidential Young Investigator Award (1985–1990)) and the Alfred P. Sloan Foundation (1985–1989).

Supplementary Material Available: Full characterization for the models **1**, **2**, and **3** are provided along with representative cyclization procedures (8 pages). Ordering information is given on any current masthead page.

Metal-Promoted Carbon–Carbon Bond Formation in the Gas Phase: Reaction of Iron Carbonyl Cations with Allyl Chloride

Hélène Mestdagh* and Christian Rolando

Ecole Normale Supérieure, Département de Chimie
UA 1110 du CNRS, Laboratoire de l'Activation Moléculaire
24 rue Lhomond, 75231 Paris, Cedex 05, France

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Gaseous transition-metal ions, bare[1] or bearing ligands,[2] have been shown to be extremely reactive with various organic compounds; for example, group 8 metal cations are able to cleave C–H and C–C bonds of alkanes.[3] However, contrary to solution organometallic chemistry, gas-phase organometallic chemistry includes relatively few examples of carbon–carbon bond formation.[4] We report here our first results concerning the $Fe(CO)_n{}^+$-allyl chloride (3-chloro-1-propene) system, in which a new type of C–C bond formation is encountered.

The reactivity of each $Fe(CO)_n{}^+$ ion (n = 0–5) with allyl chloride was studied by using a MS/MS/MS multiquadrupole spectrometer, described elsewhere,[5] with the following configuration: (i) source, electron impact on $Fe(CO)_5$; (ii) first quadrupolar analyzer, selection of $Fe(CO)_n{}^+$ reagent ion; (iii) first collision cell, reaction with allyl chloride (ca. 1 mTorr); (iv) second quadrupolar analyzer, selection of a reaction product; (v) second collision cell, CAD of this product (collision gas; Argon, ca. 0.7 mTorr, collision energy 15–25 eV); (vi) third quadrupolar analyzer, scanning. The relatively high pressure in the first collision cell allows successive reactions.

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Table I. Primary Spectra from Reaction of $Fe(CO)_n^+$ Ions (from EI on $Fe(CO)_5$) with Allyl Chloride, Percent of Total Reaction for Each Important Product Ion,[a] and Approximate Overall Rate Constants

	reactant ion						
product ion (*m/z*)	Fe^+	Fe^{+b}	$FeCO^+$	$Fe(CO)_2^+$	$Fe(CO)_3^+$	$Fe(CO)_4^{+c}$	$Fe(CO)_5^+$
$C_3H_5^+$ and products[d]	83	89	53	23	7	2 (1)	1
$C_6H_{10}^{\bullet+}$ (82), $C_5H_7^+$ (67)[e]	7	6	16	33	37	13 (9)	5
$Fe(CO)_{n-1}^+$			3	6	7	12 (15)	51
$FeCl^+$ (91.93)	4	3	2	0	0	0 (0)	0
$FeC_3H_5Cl^+$ (132, 134)	3	1	15	31	27	7 (11)	3
$FeC_4H_5ClO^+$ (160, 162)			0	0	8	24 (8)	11
$FeC_6H_9Cl^+$ (172, 174)	1	0	3	4	7	3 (1)	1
$FeC_6H_{10}Cl_2^+$ (208, 210, 212)	0	0	0	0	5	34 (53)	16
rate constant (in ms^{-1} $mTorr^{-1}$)[f]	6	*g*	14	17	7	35	*g*

[a] Because of minor reaction pathways, not included here the sum of the values corresponding to a given reactant ion is generally slightly less than 100. [b] From FAB source. [c] In parentheses, values obtained when adjusting the energy of reacting ions so as to optimize the $FeC_6H_{10}Cl_2^+$ yield. [d] Sum of the abundances of $C_3H_5^+$ (*m/z* 41) ion and its products of reaction with allyl chloride: *m/z* 55, 75, 79, 81, 89, 95, and 115 ions. [e] $C_5H_7^+$ ion arises from $C_6H_{10}^{\bullet+}$ cleavage (see text). [f] Determined from kinetic studies: allyl chloride pressure 0.1–1 mTorr, confinement time 0.06–1.4 ms. [g] Not determined.

In the first step the second analyzer was left transparent and the second collision cell empty, in order to get the primary $Fe(CO)_n^+$-allyl chloride reaction spectra. These spectra, summarized in Table I, exhibited very different patterns depending on the number of CO ligands born by the reagent ion. The reactions were also performed at variable reaction time under ion confinement conditions,[6] allowing us to determine their rate constants (Table I).

For $n = 0$ (bare Fe^+ ion) the spectrum was very similar to the reaction spectrum of source-generated $C_3H_5^+$ ion and allyl chloride; this indicates the following reaction scheme, which was also corroborated by ion rejection experiments.[7]

$$Fe^+ + C_3H_5Cl \xrightarrow{-FeCl} C_3H_5^+ \xrightarrow{C_3H_5Cl} C_6H_9^+,\ C_6H_7^+\ \ldots$$
$$\qquad \searrow \xrightarrow[-C_3H_5^{\bullet},\ \text{minor}]{} FeCl^+$$

This reactivity is not surprising considering the known reactions of alkyl halides with Fe^{+}[8] or other[2c,8,9] transition-metal ions; apart from dehydrohalogenation, which when possible is the major reaction pathway, alkyl cation formation[2c,8b,9] as well as MX^+ formation[8,9a] have been reported. Increasing n allows fixation of one and then two allyl chloride molecules to the metal atom, accompanied with departure of CO molecules. The major iron-containing product ion is thus $FeC_3H_5Cl^+$ for $n = 1$–3 and $FeC_6H_{10}Cl_2^+$ for $n = 4$. According to the confinement experiments, the latter is formed through $Fe(CO)C_3H_5^+$ and $Fe(CO)_2C_3H_5^+$ intermediates. Related "replacement" reactions of one or two CO ligands of metal carbonyl ions by an alkyl chloride molecule have been described.[2a,c,8] $Fe(CO)_5^+$ ion is much less reactive[2a] and undergoes mainly CO loss. Ion $C_6H_{10}^{\bullet+}$, along with its fragmentation product $C_5H_7^+$, was always found in variable proportions. This ion, which is not a product of $C_3H_5^+$ reaction with C_3H_5Cl, should arise from an allyl coupling reaction in an iron complex ion. Its main precursors are likely $FeC_3H_5^+$ and $Fe(CO)C_3H_5^+$ ions.

The CAD spectra of the most significant products of the preceding reactions were then recorded, giving the following results.

$$\begin{aligned} C_6H_{10}^{\bullet+}\ (m/z\ 82) &\rightarrow C_5H_7^+\ (m/z\ 67)\ \ 66\% \\ &\searrow C_4H_6^{\bullet+}\ (m/z\ 54)\ \ 28\% \\ &\searrow C_3H_5^+\ (m/z\ 41)\ \ 6\% \end{aligned}$$

This spectrum is very similar to the fragmentation pattern of hexadiene radical ions,[10] as expected if $C_6H_{10}^{\bullet+}$ is the coupling product of two C_3H_5 units. This pattern is unfortunately not sensitive to the position of the double bonds.

$$\begin{aligned} FeC_3H_5Cl^+\ (m/z\ 132, 134) &\rightarrow FeCl^+\ (m/z\ 91{,}93) + C_3H_5^{\bullet}\ \ 28\% \\ &\searrow FeC_3H_4^+\ (m/z\ 96) + HCl\ \ 62\% \\ &\searrow C_3H_5^+\ (m/z\ 41) + FeCl\ \ 10\% \end{aligned}$$

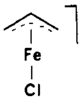
This spectrum is very different from that reported for Fe(propene)$^+$ ion, in which the only fragmentation is propene loss.[11] Absence of C_3H_5Cl loss as well as C_3H_5 and FeCl losses indicate Fe^+ insertion into the carbon–halogen bond, as observed in the case of methyl halides.[8] The relative importance of HCl elimination decreases with increasing collision energy, as expected for a rearrangement reaction as opposed to simple cleavages.[12] $FeC_3H_4^+$ ion, possibly an allene complex, was also detected in primary reaction spectra as a minor product; its CAD showed C_3H_4 loss as only fragmentation. Thus structure **1** can reasonably be assigned to $FeC_3H_5Cl^+$ ion, since π-allyl complexes of iron[13] and other metals[13,14] are known in the gas phase.

$$FeC_4H_5ClO^+\ (m/z\ 160, 162) \rightarrow FeC_3H_5Cl^+\ (m/z\ 132, 134) + CO$$
$$\downarrow$$
$$\text{secondary fragmentation:identical as above}$$

Formation of **1** shows that no CO insertion occurred in this complex, which can thus be represented by structure **2**.

$$\begin{aligned} \underset{(m/z\ 208,\ 210,\ 212)}{FeC_6H_{10}Cl_2^+} &\rightarrow \underset{\text{and fragments}}{C_6H_{10}^{\bullet+}\ (m/z\ 82)} + FeCl_2\ \ 77\% \\ &\searrow \underset{(m/z\ 132,\ 132\text{–}134,\ 134)}{FeC_3H_5Cl^+} + C_3H_5Cl\ \ 23\% \end{aligned}$$

Formation of a C_6 fragment indicates that a carbon–carbon bond has been formed between the two C_3 units incorporated in the $FeC_6H_{10}Cl_2^+$ complex, suggesting a (hexadiene)$FeCl_2^+$ structure (**3** or double bond position isomer). However, this



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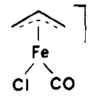

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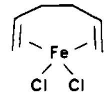

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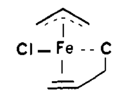

4

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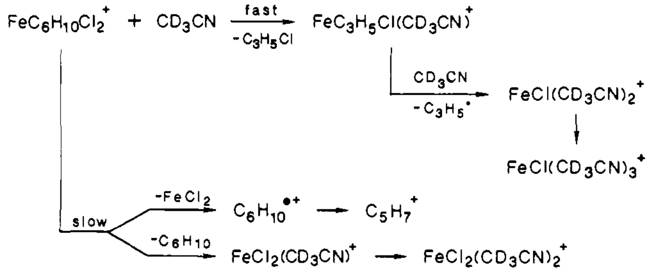
structure is not consistent with the observed allyl chloride loss, which may arise from structure **4**. Thus we conclude that $FeC_6H_{10}Cl_2^+$ ion is actually a mixture of two complexes **3** and **4**. In order to test this hypothesis, ligand exchange was attempted: $FeC_6H_{10}Cl_2^+$ was submitted to reaction with acetonitrile or trideuterated acetonitrile in the second collision cell, at a variable reaction time. The following reaction sequences were observed.



$FeC_3H_5Cl(CD_3CN)^+$ ion, deriving from rapid replacement of allyl chloride by acetonitrile in structure **4**, leads successively to $FeCl(CD_3CN)_2^+$ and $FeCl(CD_3CN)_3^+$ ions. After a short time (ca. 0.2 ms) the sum of the relative intensities of these three ions remained constant and equal to approximately 40% of the total ion current. Therefore the m/z 208 ion mixture reacted with acetonitrile should contain ca. 40% of structure **4**. The remaining slower reactions of m/z 208, involving either $C_6H_{10}^{\bullet+}$ formation or replacement of neutral C_6H_{10} with acetonitrile, are in good agreement with structure **3**. **4** → **3** isomerization reactions will now be attempted.

The reactivity of methallyl chloride with iron complexes was also investigated: with $Fe(CO)_n^+$ it is the same as that of allyl chloride. With $FeC_3H_5Cl^+$ no significant ligand exchange was observed, as expected from structure **1**; the major reaction was chloride abstraction.

$$FeC_3H_5Cl^+ + C_4H_7Cl \rightarrow C_4H_7^+\ (m/z\ 55) + C_3H_5FeCl_2$$
$$C_4H_7Cl \hookrightarrow C_8H_{13}^+\ (m/z\ 109)$$

Ion $FeC_6H_{10}Cl_2^+$ gave the expected rapid but incomplete substitution of one allyl chloride ligand by methallyl chloride, followed however by complex reactions.

The coupling reaction occurring within the $FeC_6H_{10}Cl_2^+$ complex and leading after fragmentation to hexadiene radical cation is analogous to the transition-metal-promoted coupling of allylic halides in solution (Corey reaction).[15] Interestingly, occurrence of this solution-like reaction requires the presence of several ligands on the starting iron complex ion. Further investigation is in progress to determine the scope of this reaction concerning the nature of the metal ion and ligands as well as of the organic halide.

Acknowledgment. We are indebted to the Ministère de l'Education Nationale (Ecole Normale Supérieure and Grant "Action Recherche Universitaire Entreprise") and to the Centre National de la Recherche Scientifique for their financial support of this work. We thank Dr. Nicole Morin for helpful technical assistance and Daniel Jaouen for writing the software for the instrument. The efficient technical assistance of the Nermag staff is gratefully acknowledged.

Registry No. 1, 119909-88-5; **3**, 119909-89-6; **4**, 119909-90-9; Fe^+, 14067-02-8; $FeCO^+$, 35038-14-3; $Fe(CO)_2^+$, 35038-15-4; $Fe(CO)_3^+$, 35038-16-5; $Fe(CO)_4^+$, 35038-17-6; $Fe(CO)_5^+$, 59699-78-4; allyl chloride, 107-05-1.

Supplementary Material Available: Experimental spectra for all the processes mentioned in the text (primary reaction or CAD) (34 pages). Ordering information is given on any current masthead page.

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The Unusually Robust P-H Bond in the Novel Cation $H\overline{P(NMeCH_2CH_2)_3N}^+$

C. Lensink, S. K. Xi, L. M. Daniels, and J. G. Verkade*

Gilman Hall, Department of Chemistry
Iowa State University, Ames, Iowa 50010

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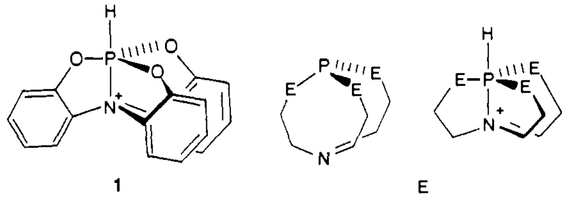
It was reported recently on the basis of NMR solution data that the phosphatrane cation **1** is unstable and was therefore not isolated.[1] In earlier publications from our laboratories, we observed, on the other hand, that the unstable prophosphatrane **2** readily protonates to form the stable cation **3**.[2-4] Here we show that in contrast to **2**, compound **4** is stable and is capable of deprotonating a variety of weak acids, including water, to form the unusually stable cation **5**.



1

E
2 O 3
4 NMe 5

Cation **5** is prepared as the chloride by adding a solution of $(HMeNCH_2CH_2)_3N$[5] (1.67 g, 11.4 mmol) in CH_2Cl_2 (20 mL), over a period of 5 min to a stirred solution of $ClP(NMe_2)_2$ (1.76 g, 11.4 mmol) and Et_3N (1.5 g, 15 mmol) in CH_2Cl_2 (30 mL). Stirring at room temperature for 1 h followed by removal of the solvent and Et_3N afforded **5** as the chloride in quantitative yield. The salt was recrystallized from hexane/chloroform at −20 °C to give an 82% yield of the product as a colorless crystalline solid.[6] Treatment of **5** (Cl^-) with $AgBF_4$ in CH_2Cl_2 gave the BF_4^- salt in quantitative yield. The ^{31}P NMR chemical shift of −10.6 ppm for **5** is indicative of five-coordinate phosphorus,[2,7] as is its one-bond H–P coupling constant of 491 Hz (**3**, 794 Hz;[2] **1**, 849 Hz[1]). The existence of an N_{ax}–P bond in **5** in solution is suggested by the observation of substantial $PN_{ax}CH_2$ coupling (4.7 Hz) and the observation of two-bond $PN_{ax}C$ coupling (6.1 Hz). These couplings are absent in prophosphatranes **2**[3] and **4**.[5] The structure of **5** was confirmed for the BF_4^- salt by X-ray crystallographic means (Figure 1).[8] Although the H–P hydrogen in **5**(BF_4^-) could not be located, the sum of the NPN angles in the equatorial plane (358.9 (4)°), the nearly right-angle relationship of the N_{ax}–P bond with the N_{eq}–P linkages (average 86.3 (4)°), the detection of the ^1H–^{31}P coupling in solution, and the directionality of the N_{ax} lone

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(6) NMR data: ^{31}P ($CDCl_3$) δ −10.6; ^1H ($CDCl_3$) δ 2.61 (9 H, d, CH_3, $^3J_{PH}$ = 17.4 Hz), δ 3.03 (6 H, dt, $N_{ax}CH_2$, $^3J_{PH}$ = 11.0 Hz, $^3J_{HH}$ = 6.2 Hz), δ 3.58 (6 H, dt, $N_{eq}CH_2$, $^3J_{PH}$ = 4.7 Hz, $^3J_{HH}$ = 6.2 Hz), δ 5.20 (1 H, d, $^1J_{PH}$ = 491 Hz); ^{13}C ($CDCl_3$), δ 34.4 (d, CH_3, $^2J_{PC}$ = 17.1 Hz), δ 41.3 (d, $N_{ax}CH_2$, $^2J_{PC}$ = 6.1 Hz), δ 47.3 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 7.3 Hz).

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(8) Crystal data: space group $Cmc2_1$, a = 8.7251 (5) Å; b = 12.3824 (7) Å, c = 13.1330 (7) Å, V = 1418.9 (2) Å^3, Z = 4, d_{calcd} = 1.423 g/cm^3, μ (MoKα) = 2.24 cm^{-1}; 897 unique reflections for $2 < \theta < 25°$, 760 observed ($F_o^2 > 3\sigma(F_o^2)$). The choice of the acentric space group was suggested by intensity statistics and was confirmed by successful refinement of the structure. The structure was solved by direct methods. Since the phosphatrane cage resides on a crystallographic mirror plane, a slight disorder arises from the possible orientations of atoms C(3), C(6), and C(7). The occupancies of the two orientations of the BF_4^- ion refined to 56.1 (5)% for the major orientation. Refinement of 113 parameters converged with agreement factors of the following: $R_1 = \Sigma|F_o - F_c|/\Sigma F_o$ = 0.0887 and $R_2 = \mathrm{sqrt}[\Sigma w(F_o - F_c)^2/\Sigma w(F_o^2)]$ = 0.1189. The refinement was carried out with the SHELX-76 package.

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