

# Four-membered rings from isocyanides: Developments since the mid 1980s

Dietrich Moderhack

*Institute of Medicinal and Pharmaceutical Chemistry, Technical University of Braunschweig  
D-38106 Braunschweig, Germany, Beethovenstraße 55  
E-mail: [d.moderhack@tu-bs.de](mailto:d.moderhack@tu-bs.de)*

**Dedicated to Professor Rosa M. Claramunt on the occasion of her 65<sup>th</sup> birthday**

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## Abstract

Reactions of isocyanides with open-chain and cyclic substrates leading to four-membered rings are reviewed. The survey is intended to be illustrative rather than encyclopedic.

**Keywords:** Isocyanides, cyclization, insertion, heterocycles, element-organic rings

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## 1. Introduction

Within the wide area of cyclizations involving the isocyano group the direct formation of four-membered rings constitutes an especially intriguing process because of elements of serendipity. The first discoveries date back to the 1960s and were summarized at the end of the decade.<sup>1</sup> The period till 1985, however, proved prolific to such an extent as to warrant a second review.<sup>2</sup> Since that time again new results have emerged in great number; this may justify the present survey.<sup>3</sup> Viewing the rich material, two features stand out: (i) The ring-forming principles have almost trebled so as to exclude an introductory graphic of the kind shown in ref.<sup>2</sup>; (ii) regarding the type of products, a plethora of element-organic rings have arisen.<sup>4</sup>

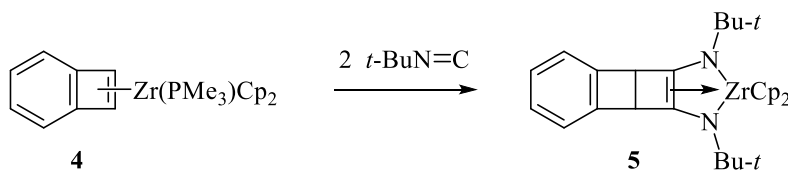
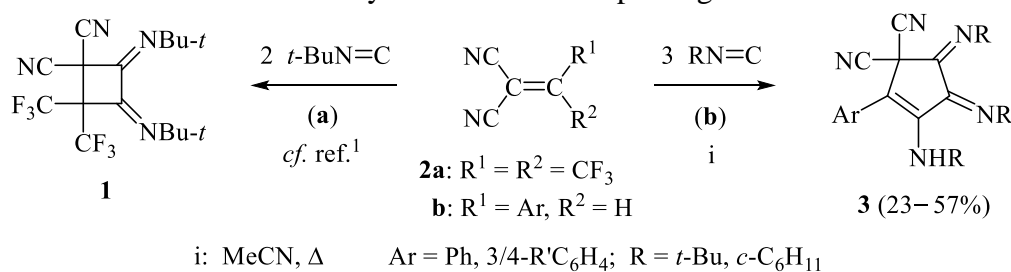
Adhering to style and format of the earlier review,<sup>2</sup> presentation of all new material will be arranged according to starting compounds rather than to products or actual mechanisms.

## 2. Reaction of isocyanides with open-chain substrates

### 2.1. [1+1+2] Cycloaddition of isocyanides to double and triple bond systems

*Alkenes*: While a methylenemalononitrile bearing two acceptor groups like the derivative **2a** reacts with *tert*-butyl isocyanide to produce the cyclobutanediimine **1** (Scheme 1),<sup>1</sup> benzylidene analogs (even though substituted with a nitro or fluoro group at the phenyl ligand) were shown to take up three molecules of the isocyanide to yield the five-membered ring **3** instead.<sup>5</sup>

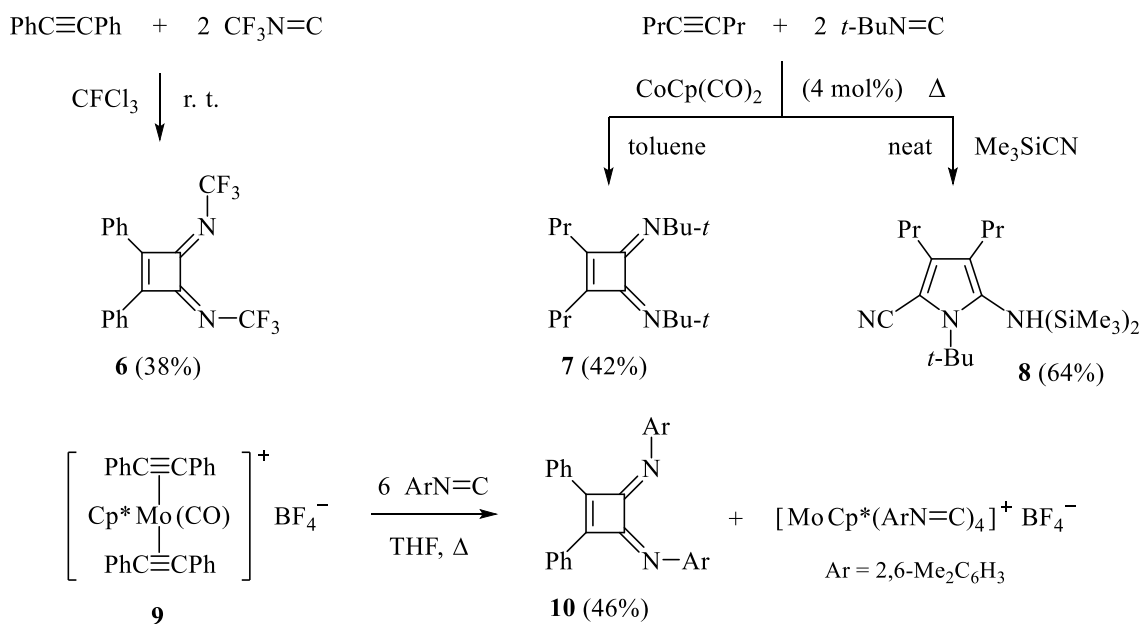
Though not being an open-chain substrate, the behavior of the benzocyclobutadiene complex **4** may be compared to that of **2a**. When two equivalents of *tert*-butyl isocyanide were added to **4**, the reagent underwent smooth insertion into both Zr–C bonds to eventually afford the Dewar-naphthalene **5**, the structure of which was established by X-ray diffraction.<sup>6</sup> Double insertion of *tert*-butyl isocyanide had been observed before also with the cyclobutene analog of **4**, but in that case the carbon atoms of the two isocyanides did not couple to give a four-membered ring.<sup>7</sup>



Scheme 1

*Alkynes*: Open-chain representatives devoid of an acceptor or donor group are usually inert towards isocyanides. As an exception, a [1+1+2] cycloaddition took place very readily when diphenylethyne was treated with trifluoromethyl isocyanide to afford the cyclobutenediimine **6** (Scheme 2). The structure of this material was determined by an X-ray structure analysis, showing that the imino functions are *E* and *Z* configured. Traces of a (mono)ketone arise unless the solvent is rigorously dried.<sup>8</sup> Similar reactions of this isocyanide were reported – but without experimental details – for but-2-yne and ethoxyethyne, whereas hexafluorobutyne and fluoroalkenes were said to be inert.<sup>9</sup>

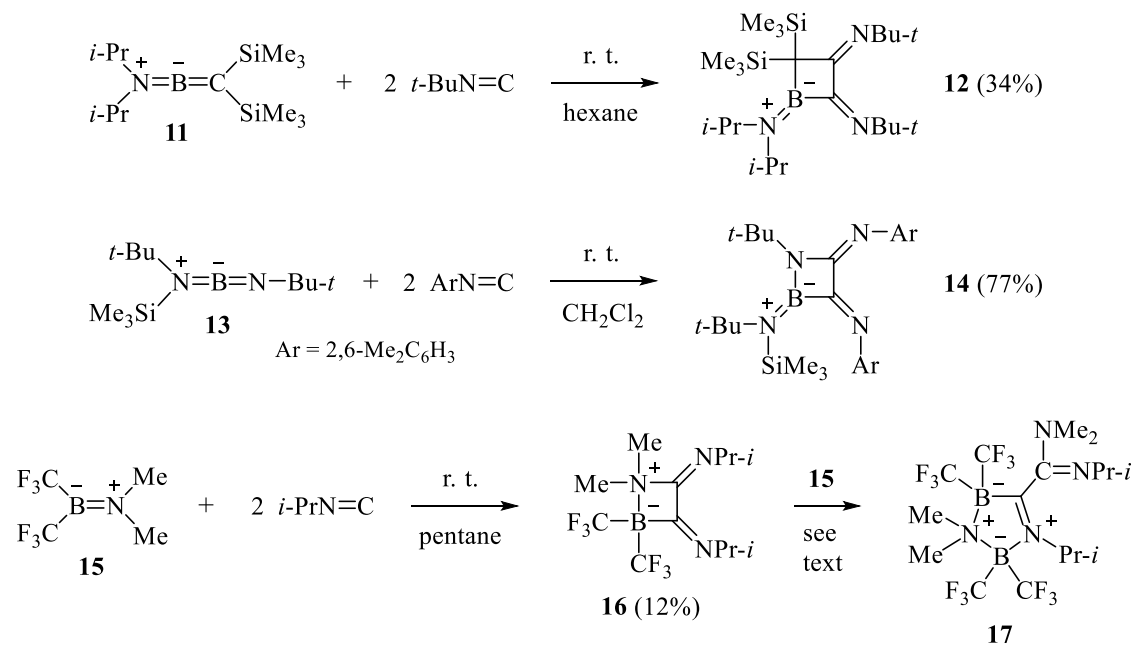
However, transition metal-induced [1+1+2] cycloadditions are relatively frequent (*cf.* ref.<sup>2</sup>); more recent examples include the following: (i) When oct-4-yne was heated with *tert*-butyl isocyanide and a catalytic amount of dicarbonylcyclopentadienylcobalt(I), the cyclobutenediimine **7** was obtained.<sup>10</sup> Yet, on adding – as a fourth component – trimethylsilyl cyanide (which equilibrates with the isocyanide *in situ*), the pyrrole **8** resulted (or its *N*-unsubstituted congener if *tert*-butyl isocyanide was replaced with cyclohexyl isocyanide). (ii) When the cationic molybdenum complex **9** was treated with six equivalents of 2,6-dimethylphenyl isocyanide, alkyne–isocyanide coupling gave rise to the four-membered ring **10**.<sup>11</sup> According to the X-ray analysis, the imino groups are configured as observed earlier with the product **6**.<sup>8</sup> – For a further example following the formal [1+1+2] cycloaddition pattern, *cf.* Section 3.2.



## Scheme 2

*Alkylidene-, imino-, aminoboranes*: Compounds of the type **11** and **13** were shown to take up two isocyanide molecules very readily (Scheme 3). Treatment of the allene-type system **11** with *tert*-butyl isocyanide afforded the boretanediiimine **12**, even when using less than two equivalents of

the isocyanide.<sup>12</sup> Accordingly, action of 2,6-dimethylphenyl isocyanide on the iminoborane **13** led to the 1,2-azaboretidinediimine **14**;<sup>13</sup> the structure of the product was investigated by X-ray diffraction (a study of **12** is lacking). Analogous behavior was shown by the aminoborane **15**; the product **16**, however, was accompanied by compound **17** which resulted from attack of unconsumed **15** on the four-membered ring; its amount increased as the reaction was prolonged.<sup>14</sup>



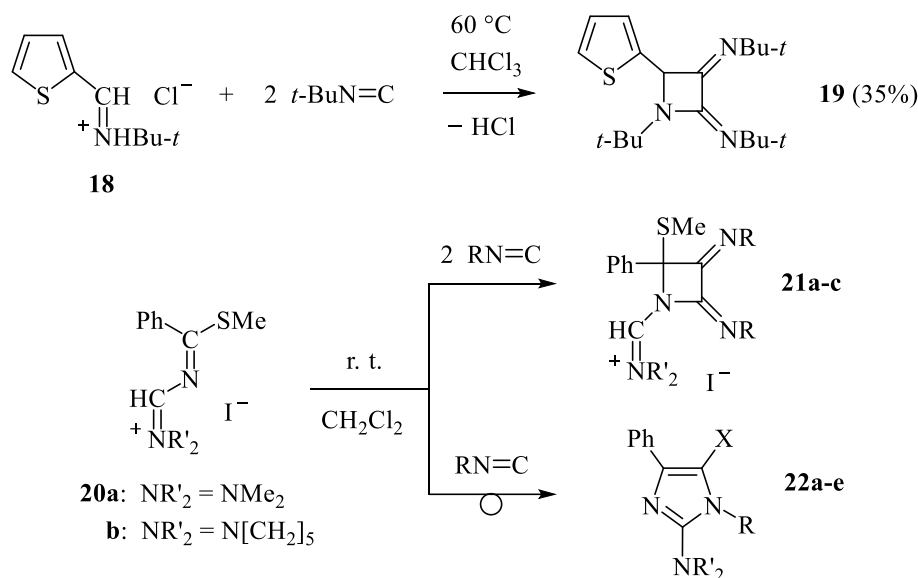
### Scheme 3

*Imines, thioimidates*: A new example for addition of two isocyanide molecules across the C=N double bond of an imine is represented by the process **18** → **19** (Scheme 4). The experiment has been carried out along with studies on  $\alpha,\beta$ -unsaturated imines which, however, afforded amino-pyrrole derivatives instead of analogs of **19**.<sup>15</sup> The thioimide unit of the salts **20a,b** could be converted into an azetidine using *tert*-butyl and isopropyl isocyanide (→ **21a-c**). But a competing reaction gave the 2-aminoimidazoles **22a-e** (by involvement of the HC=NR'<sub>2</sub> moiety of **20**).<sup>16</sup>

## 2.2. [1+2] Cycloaddition of isocyanides to double bond systems and subsequent reactions

*Diphosphenes*: Experiments with this class showed that the resultant ring type depends on the substituents (Scheme 5): **23a** reacts with methyl or trifluoromethyl isocyanide to give the stable diphosphanimines **24a,b**, whereas bis[2,4,6-tri-(*tert*-butyl)phenyl]diphosphene combines with the latter isocyanide in a 1:3 ratio to afford a 1,3-azaphospholidine derivative instead.<sup>17</sup> Three-membered rings like **24c,d** were also isolated when the metal-substituted diphosphene **23b** was reacted with phenyl or trifluoromethyl isocyanide; the same holds for the reaction of the latter component with the analogous substrate (**23c** → **24e**).<sup>18</sup> However, treatment of **23c** with several

aryl<sup>18</sup> and alkyl isocyanides<sup>19</sup> led directly to 1,3-diphosphetandiimines like **25a-f**; the transient compounds **24f-k**, being prone to P–P fission (*cf.* Section 3.1), were detected spectroscopically.

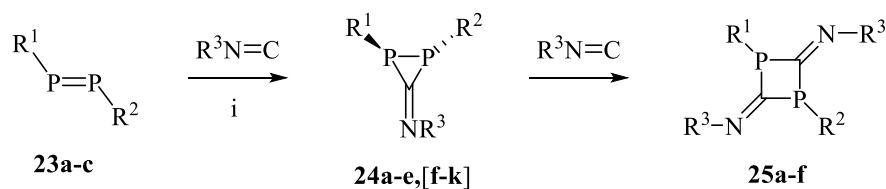


<b>21, 22</b>	R	NR' <sub>2</sub>	X	RNC (mol)	Time (h)	Products (yield, %) / from
<b>a</b>	<i>t</i> -Bu	NMe <sub>2</sub>	SMe	2	72	<b>21a</b> (8), <b>22a</b> (20), <b>22d</b> (42) / <b>20a</b>
<b>b</b>	<i>i</i> -Pr	NMe <sub>2</sub>	SMe	5	18	<b>21a</b> (18), <b>22a</b> (55) / <b>20a</b>
<b>c</b>	<i>t</i> -Bu	N[CH <sub>2</sub> ] <sub>5</sub>	SMe	5	18	<b>21b</b> (30), <b>22b</b> (44) / <b>20b</b>
<b>d</b>	<i>t</i> -Bu	NMe <sub>2</sub>	H	2	48	<b>21c</b> (16), <b>22c</b> (28), <b>22e</b> (25) / <b>20a</b>
<b>e</b>	<i>t</i> -Bu	N[CH <sub>2</sub> ] <sub>5</sub>	H	4	10	<b>21c</b> (25), <b>22c</b> (45) / <b>20b</b>

#### Scheme 4

*Silenes*: Photolysis of the acylsilane **26a** using 360-nm radiation generated the silene derivative **27a** (Scheme 6). In the presence of one equivalent of *tert*-butyl isocyanide (**a**) this compound underwent a [1+2] cycloaddition to give the siliranimine **28a** which in turn rearranged into the azasiliridine **29a**.<sup>20,21</sup> When a mixture of this material and 2,6-dimethylphenyl isocyanide (**b**) was photolyzed, the 1,3-azasiletid-2-imine **30a** resulted.<sup>22</sup> Extending the experiments to the couples **27a** + (**a**), **27b** + (**a**), and **27b** + (**b**), the expected azasiliridines **29b-d** were formed, but these compounds, while eluding isolation, reacted with unconsumed isocyanide and produced the azasiletidines **30b-d**. However, under nonphotochemical conditions (–70 °C; dark) preformed **27a** and 2,6-dimethylphenyl isocyanide (**b**) gave rise to a mixture of the compounds **29b** and **30b**; this contrasts with the behavior of **27a** towards alkyl isocyanides (*cf.* above and ref.<sup>20</sup>), which leads exclusively to the type **29**. – Detailed NMR spectroscopic investigations of the products **30a-d** have shown the occurrence of two stereoisomers each for **a** and **b**, but only one for **c** and **d**. An X-ray diffraction study of the major isomer of **30b** has revealed a *Z/E* symmetry (C=N /

C=C group) as depicted; for brevity, this stereo formula was used here for **30a,c,d** as well. Yields of **30a-d** were not disclosed throughout.<sup>22</sup>



i: 0 or 20 °C / (*n*-)pentane (for **24a-d**), 2-methylbutane (**24e**);  
20 °C / benzene (for **25a,b**), toluene (**25d**), diethyl ether (**25e**), neat (**25f**)

23	24	25	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Yield (%) <sup>c</sup>	<i>E</i> : <i>Z</i> <sup>d</sup>
<b>a</b>	<b>a</b>		C(SiMe <sub>3</sub> ) <sub>3</sub>	C(SiMe <sub>3</sub> ) <sub>3</sub>	Me	61	
	<b>b</b>		C(SiMe <sub>3</sub> ) <sub>3</sub>	C(SiMe <sub>3</sub> ) <sub>3</sub>	CF <sub>3</sub>	63	
<b>b</b>	<b>c</b>		[Fe] <sup>a</sup>	C(SiMe <sub>3</sub> ) <sub>3</sub>	CF <sub>3</sub>	31	
	<b>d</b>		[Fe]	C(SiMe <sub>3</sub> ) <sub>3</sub>	Ph	63	
<b>c</b>	<b>e</b>		[Fe]	Mes* <sup>b</sup>	CF <sub>3</sub>	54	
	<b>f</b>	<b>a</b>	[Fe]	Mes*	Ph	63	2 : 1
	<b>g</b>	<b>b</b>	[Fe]	Mes*	2-MeC <sub>6</sub> H <sub>4</sub>	48	2 : 1
	<b>h</b>	<b>c</b>	[Fe]	Mes*	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>		
	<b>i</b>	<b>d</b>	[Fe]	Mes*	C <sub>6</sub> F <sub>5</sub>	46	6 : 1
	<b>j</b>	<b>e</b>	[Fe]	Mes*	<i>c</i> -C <sub>6</sub> H <sub>11</sub>	57	2 : 1
	<b>k</b>	<b>f</b>	[Fe]	Mes*	CH <sub>2</sub> Ph	79	2 : 1

<sup>a</sup> [Fe] = FeCp\*(CO)<sub>2</sub>. <sup>b</sup> Mes\* = 2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>. <sup>c</sup> Products **24a-e** and **25a-f**, respectively (no yield for **25c**). <sup>d</sup> Two *Z* isomers observed.

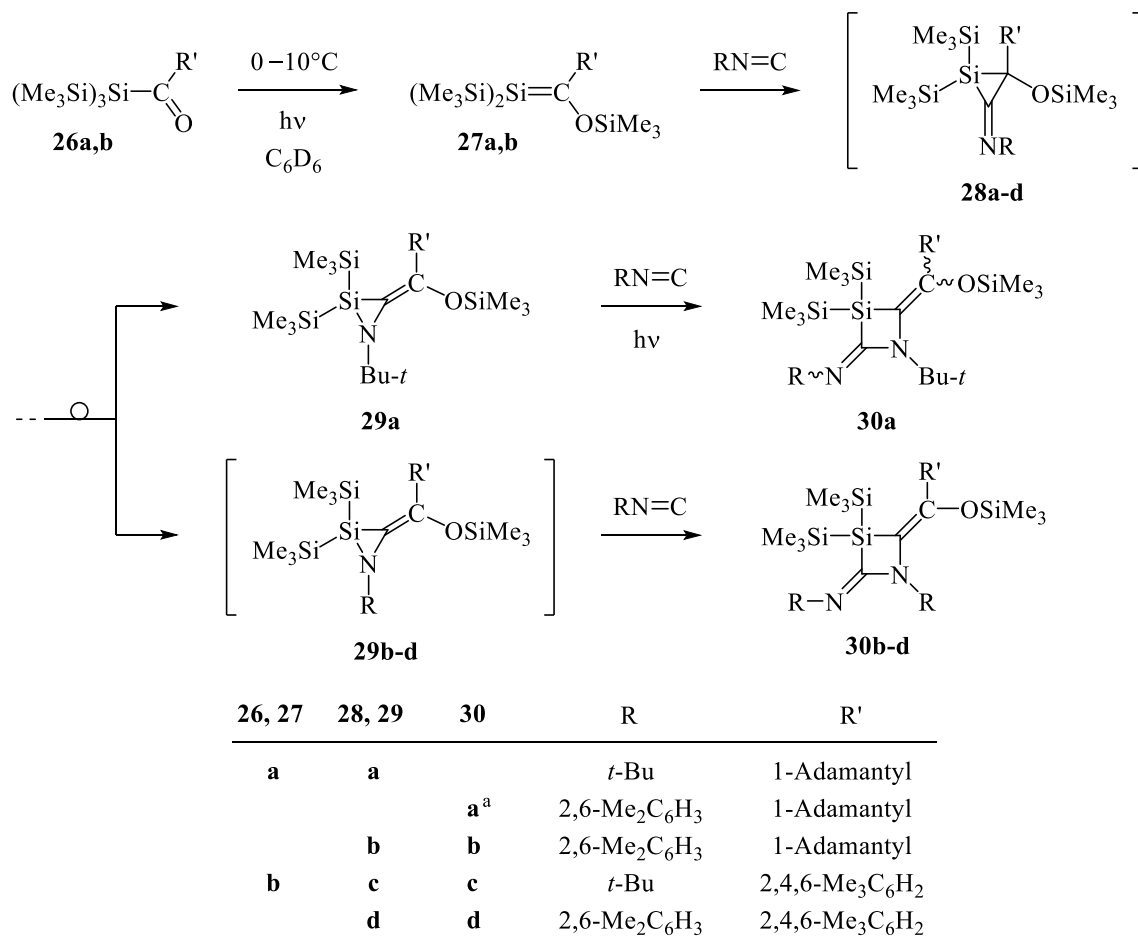
## Scheme 5

A later example of this kind of conversion constitutes the reaction of the neopentyl-substituted silene **27c**. This substrate – prepared from (dimesitylfluorosilyl)ethene and *tert*-butyllithium – gave the silazetidene **30e** on treatment with two equivalents of *tert*-butyl isocyanide.<sup>23</sup>

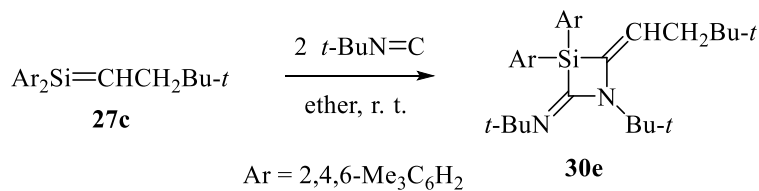
It might be added that azasiliridines related to **29** were obtained very recently from isocyanides and a disilene like R<sub>2</sub>Si=SiRPh [R = 2,4,6-(*i*-Pr)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>], but, remarkably, these products (which have a semicyclic C=Si bond instead of a C=C bond) did not undergo isocyanide insertion to give four-membered rings, *i.e.* silylidene analogs of **30**.<sup>24</sup>

*Phospha-, arsasilenes*: Unique derivatives of the type **30**, *i.e.* compounds like **32a-c**, arose quantitatively on exposure of the 'heterosilenes' **31a**<sup>25</sup> and **31b**<sup>26</sup> to mesityl and cyclohexyl isocyanide (Scheme 7). The reaction was assumed to follow the pattern of the preceding paragraph. Treatment of the products **32b,c** with hydrogen chloride (or fluoride), however, met with surprise in that arsasilene derivatives **33a,b** were isolated; X-ray crystallography served to establish the

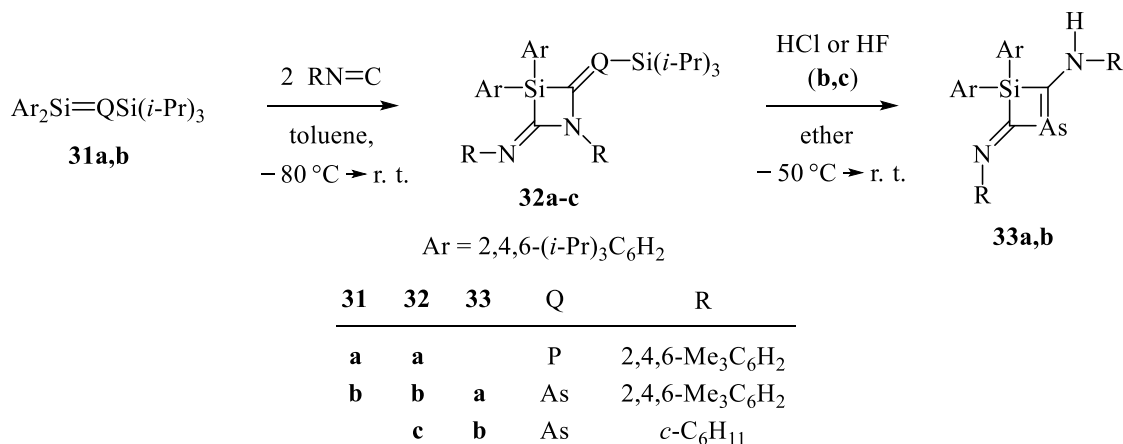
structures of both **32c** and **33b**.<sup>26</sup> Extending their ring forming experiments to 1,6-diisocyanohexane, the authors succeeded in converting **31a,b** into the corresponding macroheterocycles; of these new products, the arsa representative has also been studied by X-ray diffraction.<sup>27</sup>



<sup>a</sup> Compound **30a** isolated as mixed species of two geometric isomers in about 3:2 proportions.



Scheme 6



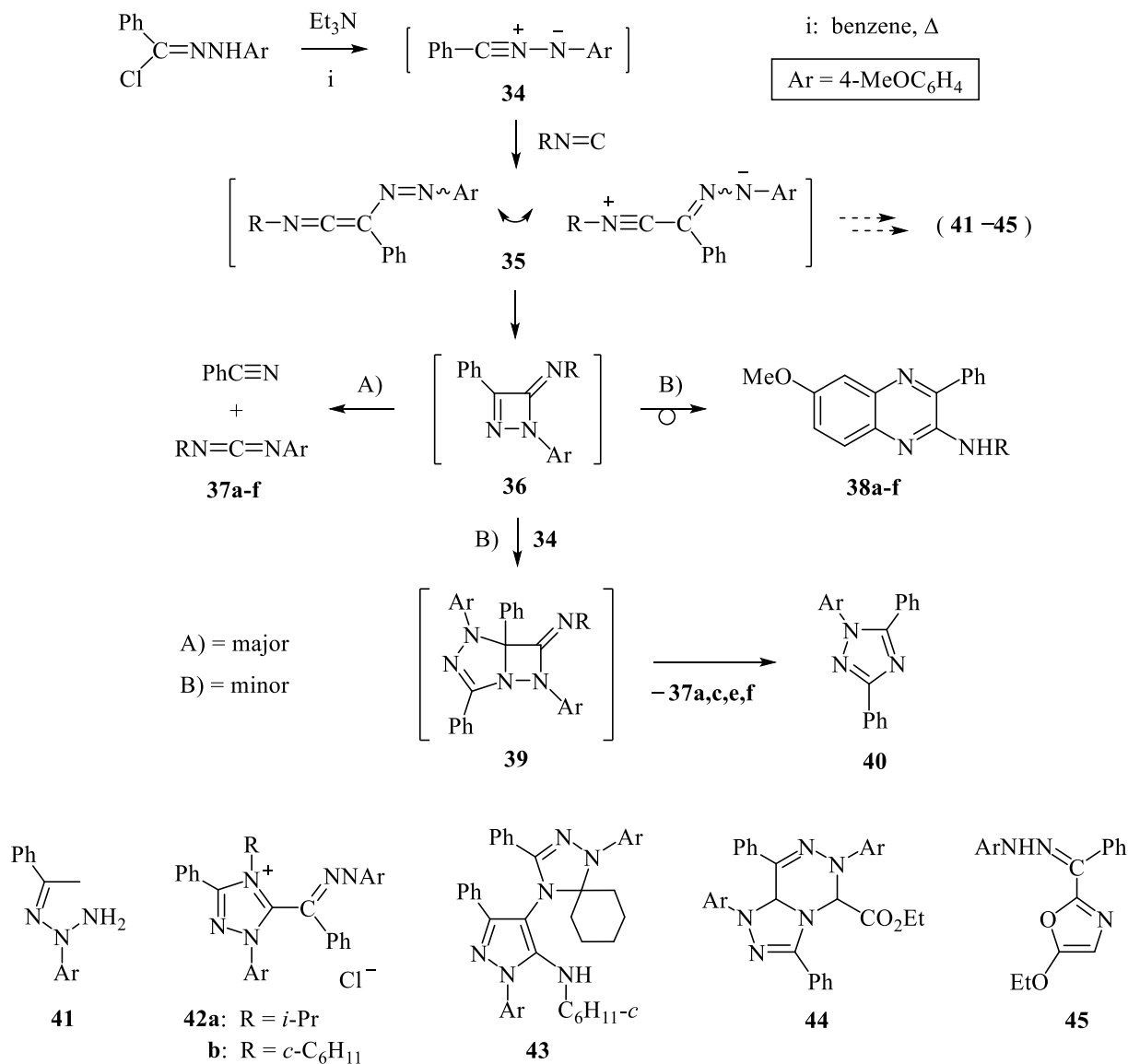
## Scheme 7

### 2.3. [1+3] Cycloaddition of isocyanides to 1,3-dipoles

*Nitrile imines*: Detailed studies on the behavior of *N*-aryl nitrile imines towards isocyanides<sup>28–32</sup> have shown that the title reaction occurred under certain conditions.<sup>29,31,32</sup> Best suited are nitrile imines bearing a donor-substituted phenyl group at the terminal nitrogen like **34**, they gave cycloadducts **36** with a wide variety of isocyanides (Scheme 8).<sup>31,32</sup> These four-membered rings, however, eluded isolation, but their formation could be inferred from products formed by [2+2] cycloreversion into benzonitrile and a carbodiimide (**37**), by ring expansion to a quinoxaline (**38**), and finally by [2+2] cycloreversion of the secondary adduct **39** into **37** and a 1,2,4-triazole (**40**). Besides these compounds products such as **41–45** were found; formally, they derive from the linear adduct **35** which in the case R = *t*-Bu could be detected spectroscopically.<sup>33</sup>

Compared to **34**, the proclivity of its *N*-phenyl analog to undergo a [1+3] cycloaddition is low,<sup>29</sup> and with Ar = 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub> there were no indications at all.<sup>32</sup> This failure applies also to nitrile imines having an acceptor group at the C-terminus like an acyl<sup>31</sup> or a 4-nitrophenyl substituent.<sup>32</sup>



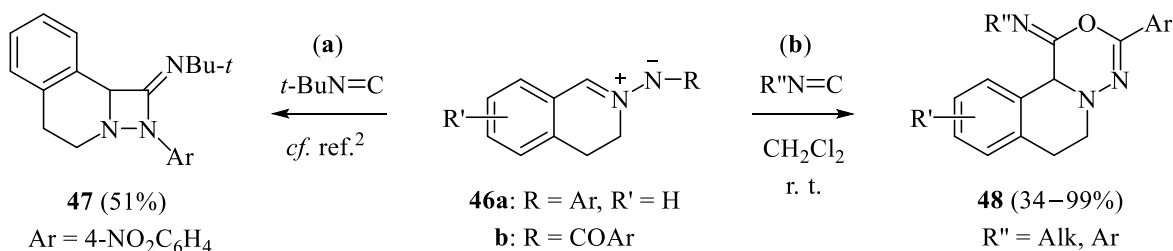


37	Yield (%) <sup>a</sup>	R	38	Yield (%)	Other / Yield (%)
a	49	<i>i</i> -Pr	a	15	40 / 2, 42a / 8
b	19	<i>t</i> -Bu	b	3	41 <sup>b</sup> / 27
c	43	<i>c</i> -C <sub>6</sub> H <sub>11</sub>	c	25	40 / 2, 42b / 10, 43 / 6
d <sup>c</sup>		CH <sub>2</sub> CO <sub>2</sub> Et	d	18	44 / 31, 45 / 7
e	37	4-MeOC <sub>6</sub> H <sub>4</sub>	e	21	40 / 6
f	62	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	f	17	40 / 5

<sup>a</sup> Yield based on the respective urea. <sup>b</sup> By elimination of isobutene from transient 1-*tert*-butyl-2-(4-methoxyphenyl)-5-phenyl-2*H*-1,2,3-triazolium. <sup>c</sup> Carbodiimide 37d apparently unstable.

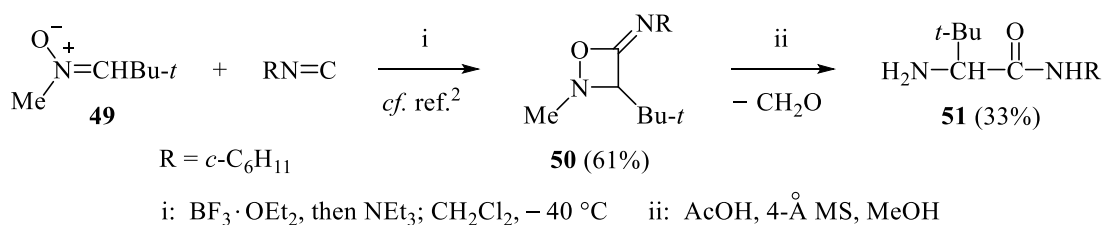
## Scheme 8

*Azomethine imines*: In contrast to the aryl functionalized CNN moiety in **46a** which, using *tert*-butyl isocyanide, was earlier cyclized to a 1,2-diazetidene ring (**47**),<sup>2</sup> the acyl group in the congener **46b**, as shown recently, confers upon the molecule a 1,5-dipolar character which led to the formation of a 1,3,4-oxadiazine cycle (**48**) (Scheme 9).<sup>34</sup>



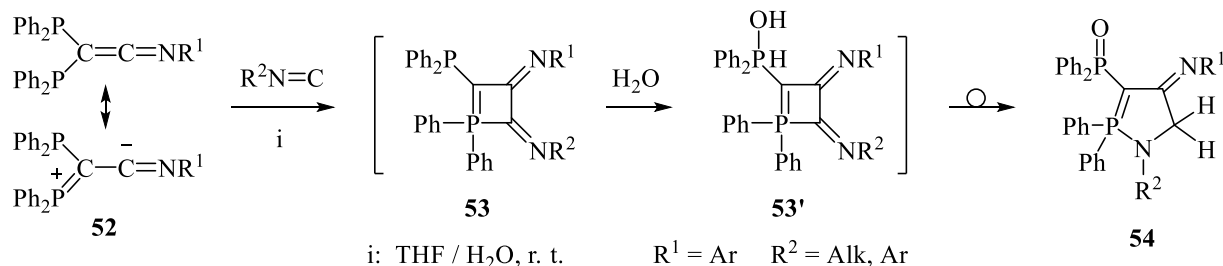
### Scheme 9

*Nitrones*: The known cyclization<sup>2</sup> of the nitron **49** with cyclohexyl isocyanide to give the 1,2-oxazetid-4-imine **50** has recently been duplicated for mechanistic purposes (Scheme 10).<sup>35</sup> To rationalize their synthesis of  $\alpha$ -oxoamides from *N*-alkylhydroxylamines and aliphatic aldehydes under the conditions of the Ugi reaction, the authors thought of **50** as one possible intermediate and submitted this model to their procedure. But, being aware of an old observation,<sup>36</sup> they confirmed that N–O cleavage in **50** occurred with deprotonation of the *N*-methyl group ( $\rightarrow$  **51**), not at C(3) which would be necessary for the production of an  $\alpha$ -oxoamide.



### Scheme 10

*Diphosphinoketenimines*: Although representing no classical 1,3-dipoles, the title substrates **52** were shown to behave as such (Scheme 11). In the presence of water they reacted with isocyanides to give compounds of the type **54** that were proposed to arise *via* four-membered rings like **53/53'**. Labeling experiments demonstrated that the oxygen and ring-attached hydrogen of **54** originate from the external water; in a rigorously dried medium no reaction occurred.<sup>37</sup>

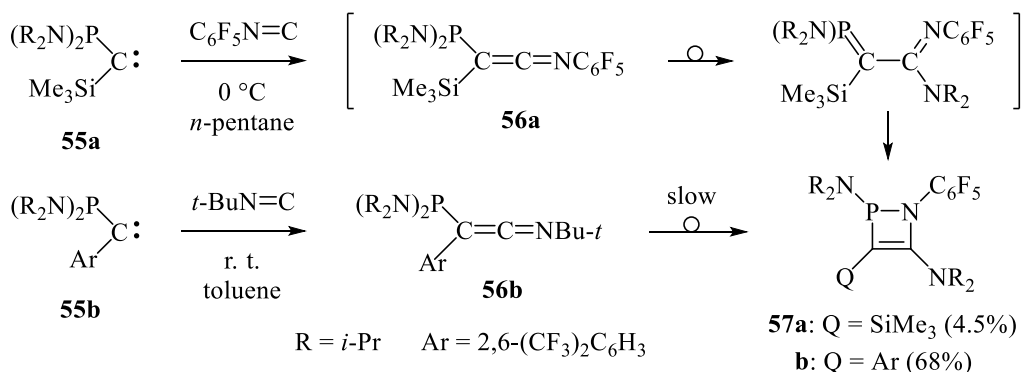


### Scheme 11

(For 1,3-dipolar behavior of metal-coordinated ketenimines, see Section 2.5.)

## 2.4. Addition of isocyanides to carbenes (including analogs) and subsequent reactions

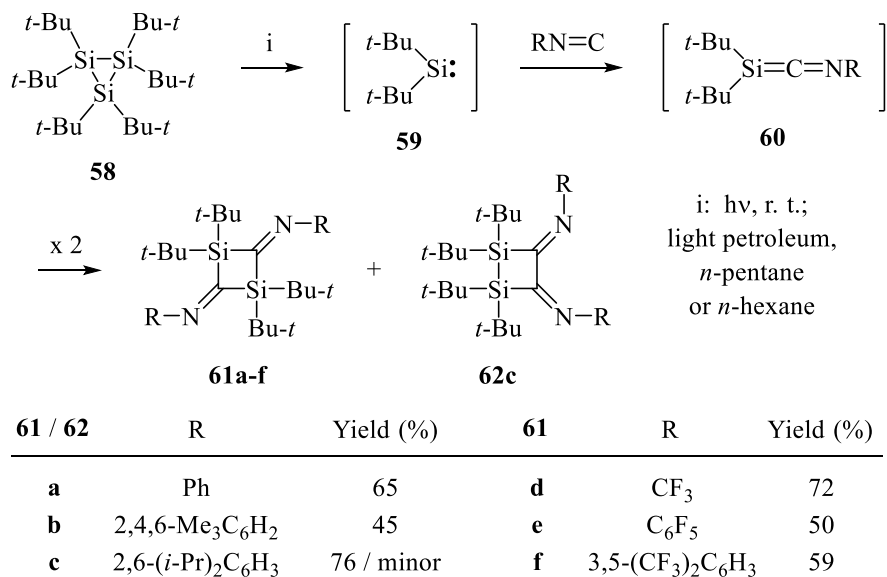
**Carbenes:** The phosphino(silyl)carbene **55a**, generated from the corresponding diazo precursor, reacted with pentafluorophenyl isocyanide to give the dihydro-1,2-azaphosphete **57a**, which was established by an X-ray analysis (Scheme 12). The process was explained to involve a transient ketenimine (**56a**) that undergoes a  $P \rightarrow C$  migration of one  $NR_2$  group, followed by electrocyclicization of the resultant 1-aza-4-phosphabutadiene.<sup>38,39</sup> When reacting the arylsubstituted carbene **55b** with *tert*-butyl isocyanide, the respective ketenimine **56b** could be characterized spectroscopically, but at room temperature it rearranged slowly into the analogous ring system **57b**.<sup>40</sup>



### Scheme 12

**Silylenes:** Photolysis of the trisilirane **58** in the presence of isocyanides has been shown to afford disiletanediimines of the type **61** and **62** (Scheme 13). These compounds arose by coupling of the silylene **59** with the isocyanide to give the silaketenimine **60** which in turn cyclodimerized. The reaction was performed with phenyl<sup>41</sup> and sterically crowded aryl isocyanides,<sup>42</sup> but also with isocyanides bearing electron-withdrawing groups.<sup>43</sup> As expected, head-to-tail cyclodimerization prevails; only when using 2,6-diisopropylphenyl isocyanide the head-to-head mode occurred too,

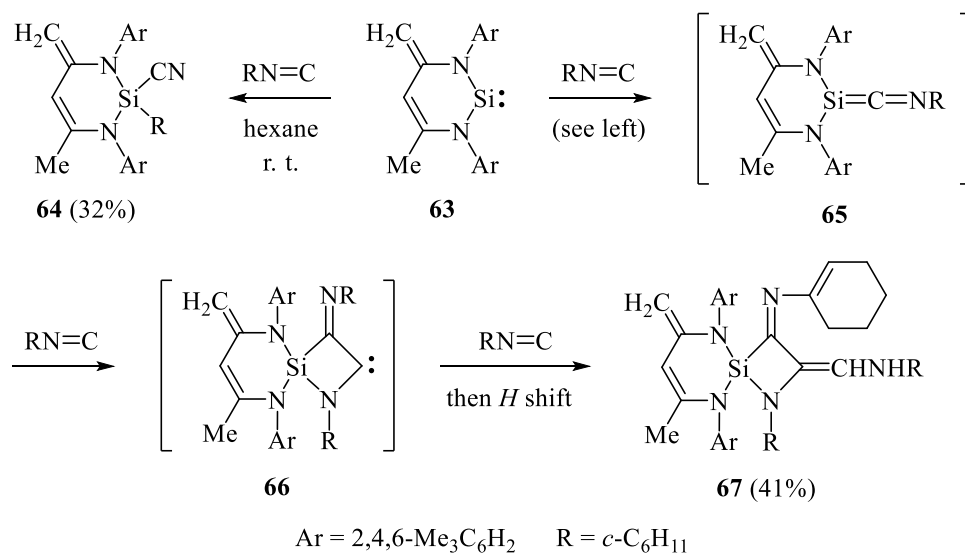
giving minor amounts of the derivative **62c**.<sup>42</sup> While no yield figure was disclosed in that work, it was later detailed that the derivatives **61c** and **62c** were isolated in a ratio of *ca.* 10:1 (regardless of the reaction conditions) and that they were not interconverted photochemically.<sup>44</sup> The molecular geometry of **61a,c,d** and **62c** has been determined by X-ray crystallography.<sup>41-43</sup>



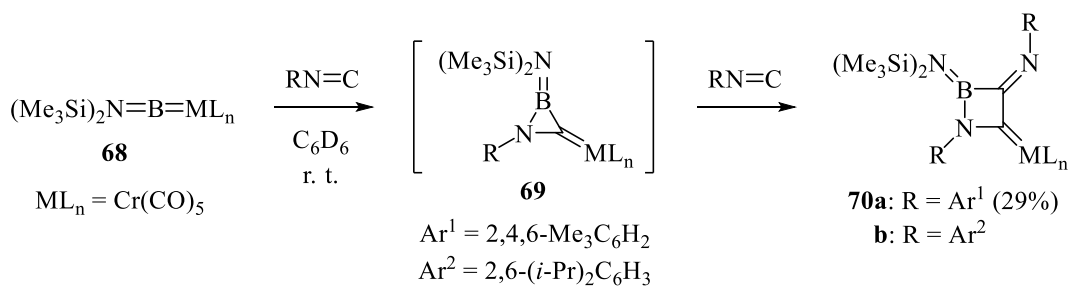
### Scheme 13

Surprising behavior was encountered with the (stable) silylene **63**. On treatment with cyclohexyl isocyanide two competing reactions occurred (Scheme 14): (i)  $\alpha$ -addition of the CN and *c*-C<sub>6</sub>H<sub>11</sub> moieties of the fragmented reagent furnished the carbonitrile **64**; (ii) linear coupling of intact isocyanide led to the silaketeneimine **65**; this intermediate, in contrast to species **60** (*cf.* Scheme 13), took up another isocyanide to generate a four-membered ring ( $\rightarrow$  **66**); stabilization of its carbene function by uptake of a third isocyanide, followed by hydrogen migration from the cyclohexylimino group, gave the product **67**, the structure of which was established by the X-ray method.<sup>45</sup>

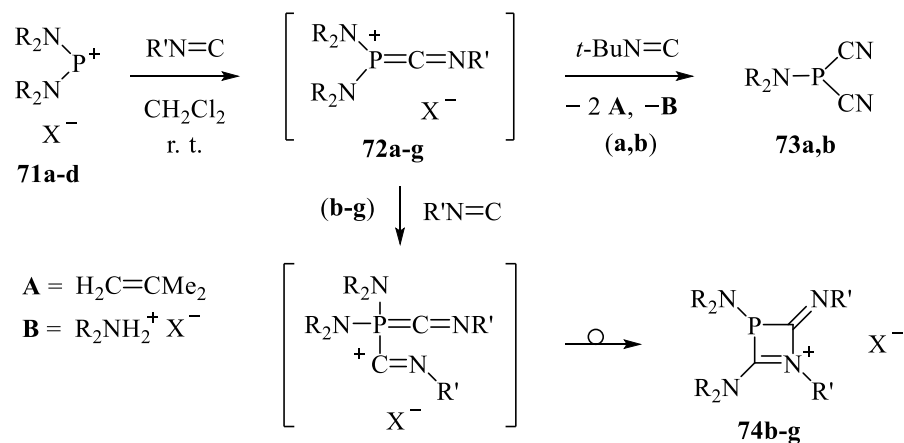
*Borylenes*: An interesting borylene-to-isocyanide transfer resulting in the final formation of the four-membered rings **70a,b** happened when the chromium complex **68** was treated with certain aryl isocyanides (Scheme 15). The reaction assumedly involved a [1+2] cycloadduct (**69**) that was susceptible to isocyanide insertion. The molecular structure of **70a** was elucidated by X-ray diffraction.<sup>46</sup>



Scheme 14



Scheme 15



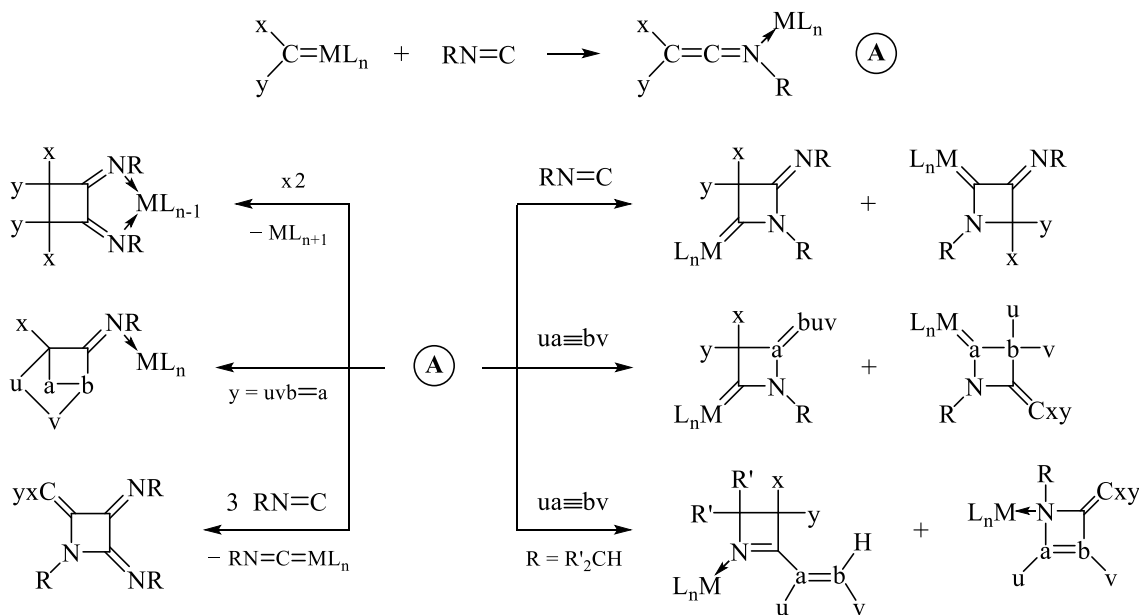
71-74	R	R'	X	Yield (%)	71-74	R	R'	X	Yield (%)
a	<i>i</i> -Pr	<i>t</i> -Bu	CF <sub>3</sub> SO <sub>3</sub>		e	Me	<i>c</i> -C <sub>6</sub> H <sub>11</sub>	CF <sub>3</sub> SO <sub>3</sub>	90
b	Et	<i>t</i> -Bu	CF <sub>3</sub> SO <sub>3</sub>	50	f	Et	<i>c</i> -C <sub>6</sub> H <sub>11</sub>	CF <sub>3</sub> SO <sub>3</sub>	80
c	Me	<i>t</i> -Bu	CF <sub>3</sub> SO <sub>3</sub>	92	g	<i>i</i> -Pr	<i>c</i> -C <sub>6</sub> H <sub>11</sub>	CF <sub>3</sub> SO <sub>3</sub>	90
d	Me	<i>t</i> -Bu	AlCl <sub>4</sub>	89					

Scheme 16

*Phospheniums (Addendum)*: Carbenoid properties are also exhibited by phosphenium salts like **71a-d** (Scheme 16). These substrates couple with alkyl isocyanides to give transient phosphaket-enimines (**72a-g**) which, depending on the substituents, react with a second molecule of isocyanide to afford either dicyanophosphine derivatives (**73a,b**) or imino-substituted dihydro-1,3-aza-phosphetium salts (**74b-g**). When the intermediate **72b** took up *tert*-butyl isocyanide, both routes were followed so as to reduce the yield of the product **74b**.<sup>47,48</sup>

## 2.5. Addition of isocyanides to Fischer carbene complexes and subsequent reactions

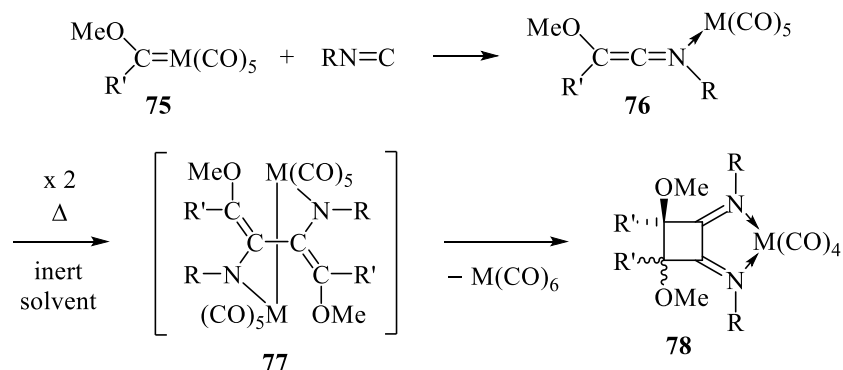
Isocyanides combine with Fischer-type carbenes to generate ketenimine complexes of the type **A** (Scheme 17). The mechanism of the process has recently been studied, showing that **A** is formed *via* a metallacyclopropanimine followed by isomerization and 1,2-metallotropic rearrangement.<sup>49</sup> Preparatively, these species have turned out to be valuable building blocks for a variety of four-, five-, and six-membered rings (for reviews, see refs.<sup>50,51</sup>). Concentrating on the first mentioned class, this section will describe applications of the synthetic principles outlined below. Beyond that, mention will be made of the ring contraction of a single [2+3] cycloadduct obtained from **A**.



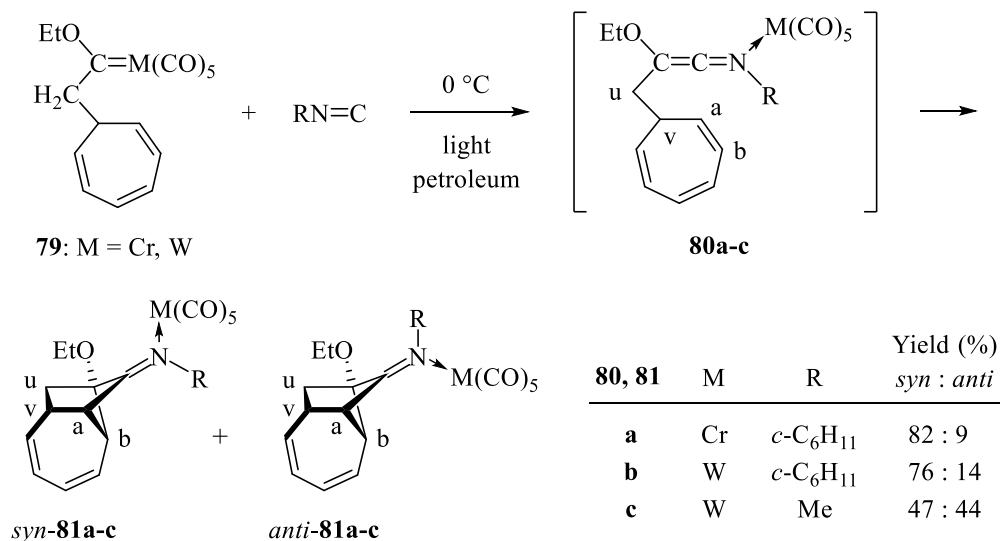
**Scheme 17**

*Dimerization*: Carbene complexes such as **75** react with alkyl isocyanides to give the corresponding ketenimine complexes **76** (Scheme 18). On being heated in an inert solvent, these coupling products slowly dimerize to afford the metal-coordinated cyclobutanediimines **78**.<sup>52-54</sup> The symmetrical [2+2] cycloaddition which is unusual for free ketenimines is template-induced and thought to proceed through an intermediate like **77**. Part of this remarkable reaction has been reviewed earlier.<sup>2</sup>

**Intramolecular cycloaddition:** Ketenimine complexes bearing an alk-3-enyl moiety at the carbon atom like the derivatives **80a-c** undergo, once generated from the precursor **79**, an intramolecular [2<sub>s</sub>+2<sub>a</sub>] cycloaddition (Scheme 18). Owing to the involvement of the cycloheptatrienyl ligand, the cyclobutanimine unit becomes part of a tricyclic system, as illustrated by the products **81a-c**. Of these materials, two stereoisomers were found; the structure of *anti*-**81c** has been determined by X-ray crystallography. Attempts to demetalate this derivative with pyridine caused fragmentation of the four-membered ring.<sup>55</sup>



R' = Me, Ph, 2-thienyl, naphthyl (unspecified); M = Cr, Mo, W; R = Me, *t*-Bu, *c*-C<sub>6</sub>H<sub>11</sub>



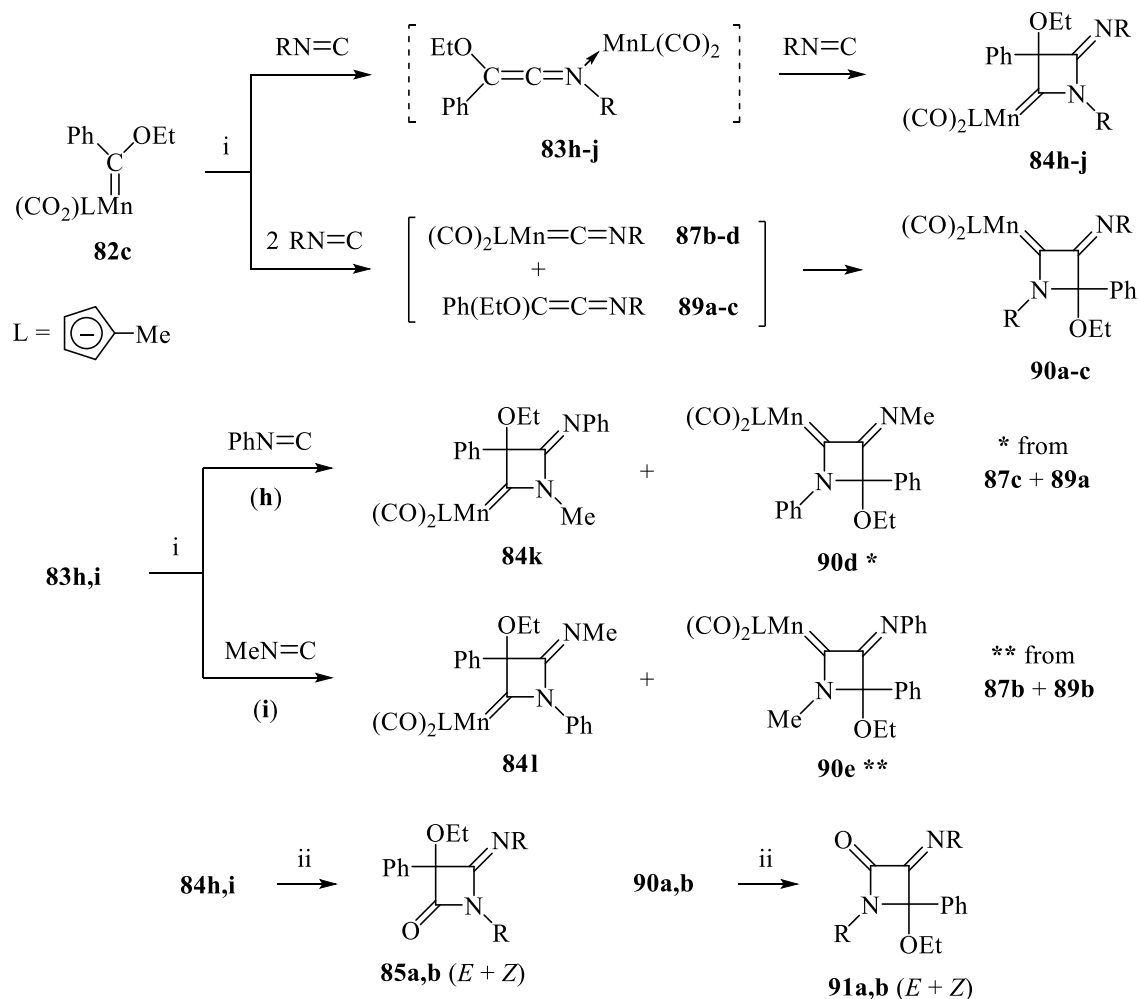
### Scheme 18

**Addition of isocyanides:** Ketenimine complexes exhibit 1,3-dipolaroid properties. Using isocyanides as dipolarophiles, 4-iminoazetid-2-ylidene complexes can arise (Scheme 19). Success and extent of this reaction depend primarily on the metal. Thus, starting from the iron carbene complex **82a**, the desired products, *e.g.* **84a-d**, were obtained in high yield regardless of the nature of the isocyanide; the intermediary ketenimine complexes **83a-d** were not observed.<sup>56,57</sup> Yet, in the





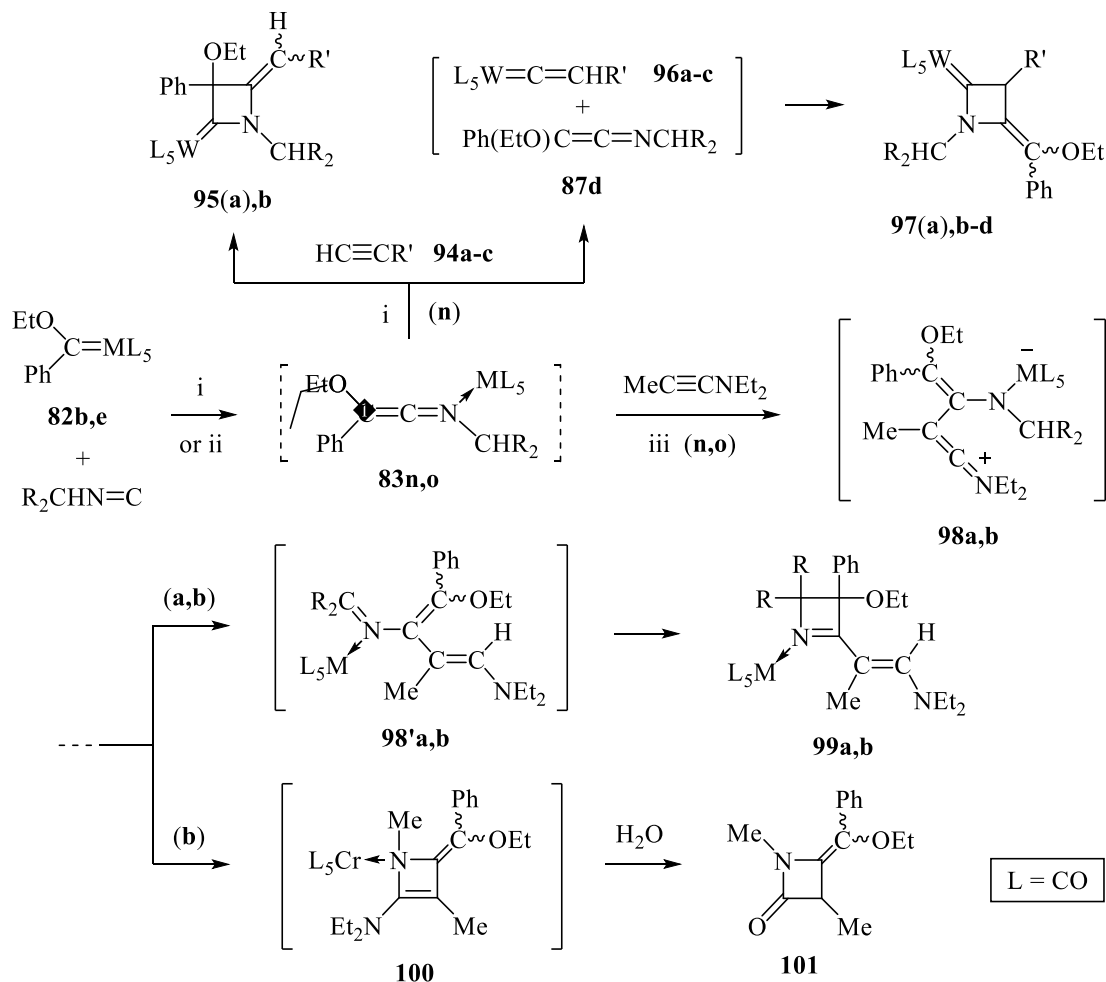
consequence of this competing process, the 'regular' products **84h-j** were accompanied by [2+2] cycloadducts like **90a-c**; the proportions varied with the conditions and the kind of isocyanide. Since the conversion **83** → **84** proceeds more slowly than the step **82c** → **83**, it was also possible to construct azetidinylidene complexes **84** (including the type **90**) from two different isocyanides; this is exemplified by the couples **84k** / **90d** and **84l** / **90e**. Representatives of both ring series such as **84h,i** and **90a,b** could be demetalated with permanganate salt to give the β-lactams **85a,b** and **91a,b**, respectively.<sup>59</sup>



<b>83, 84</b>	R	<b>87</b>	<b>89-91</b>	Yield (%) <b>84</b> / <b>90</b>	Conditions
<b>h</b>	Me	<b>b</b>	<b>a</b>	30 [4] / 15 [25]	60 °C (4 h) → 100 °C (3 h) [100 °C (4 h)]
<b>i</b>	Ph	<b>c</b>	<b>b</b>	67 [37] / 4 [10]	60 °C (4 h) → 100 °C (3 h) [100 °C (4 h)]
<b>j</b>	CH <sub>2</sub> Ph	<b>d</b>	<b>c</b>	29 / trace	100 °C (3.5 h)

Scheme 20





<b>82</b>	<b>83</b>	<b>94</b>	<b>95</b>	<b>98</b>	<b>99</b>	M	R, R	R'	Yield (%) ( <b>95</b> / <b>97</b> )	E : Z ( <b>97</b> )	Yield (%) ( <b>99</b> )
<b>b</b>	<b>n</b>	<b>a</b>	<b>a</b> <sup>a</sup>	<b>a</b>	W	[CH <sub>2</sub> ] <sub>5</sub>	SiMe <sub>3</sub>				23
<b>e</b>	<b>o</b>			<b>b</b>	Cr	H, H					13
				<b>b</b>		[CH <sub>2</sub> ] <sub>5</sub>	H		10 / 13	2 : 3	
				<b>b</b>		[CH <sub>2</sub> ] <sub>5</sub>	CH <sub>2</sub> OMe		0 / 18	1 : 2	
				<b>c</b>		[CH <sub>2</sub> ] <sub>5</sub>	Ph		0 / 28	1 : 12	

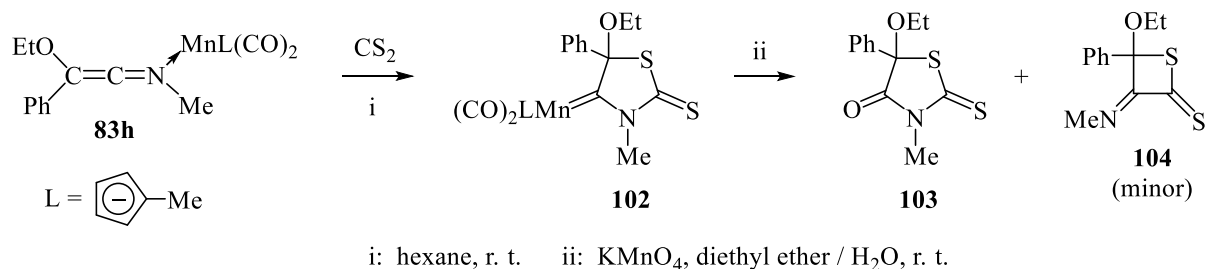
<sup>a</sup> Products **95a** and **97a** were hydrolyzed to **95b** and **97b** during work-up.

## Scheme 22

b) Ynamines: The reaction of the ketenimine complexes **83** with the electron-rich diethyl-(prop-1-ynyl)amine took an unexpected course: Treatment of **83n,o** (isolated pure) furnished the 2,3-dihydroazete complexes **99a,b** (Scheme 22). Here four atoms of the original ketenimine unit were incorporated into the product (the structure of **99b** was studied by X-ray crystallography).

Mechanistically, the reaction was understood as proceeding through an adduct of the type **98**; in this species a hydrogen transfer from the CHR<sub>2</sub> group to the central keteniminium carbon took place to generate the intermediate **98'** which underwent electrocyclization. In the case of **98b**, a second mode was operative, *i.e.* intramolecular [2+2] cycloaddition to the 1,4-dihydroazetidene complex **100** which on work-up was hydrolyzed to the β-lactam **101** (no yield).<sup>63</sup>

*Ring contraction (Addendum):* An unexpected formation of a four-membered ring was encountered when the [2+3] cycloadduct **102** from the ketenimine complex **83h** (for preparation, see Scheme 20) and carbon disulfide was oxidized with aqueous permanganate (Scheme 23). Besides the regular product – the thiazolidin-5-one **103** – small amounts of the 3-iminothietane-2-thione **104** were detected; formally, this material arose through ring contraction of 'deoxygenated' **103**. Both compounds were formed in a 20:1 ratio with a total yield of 96% (crude).<sup>64</sup>



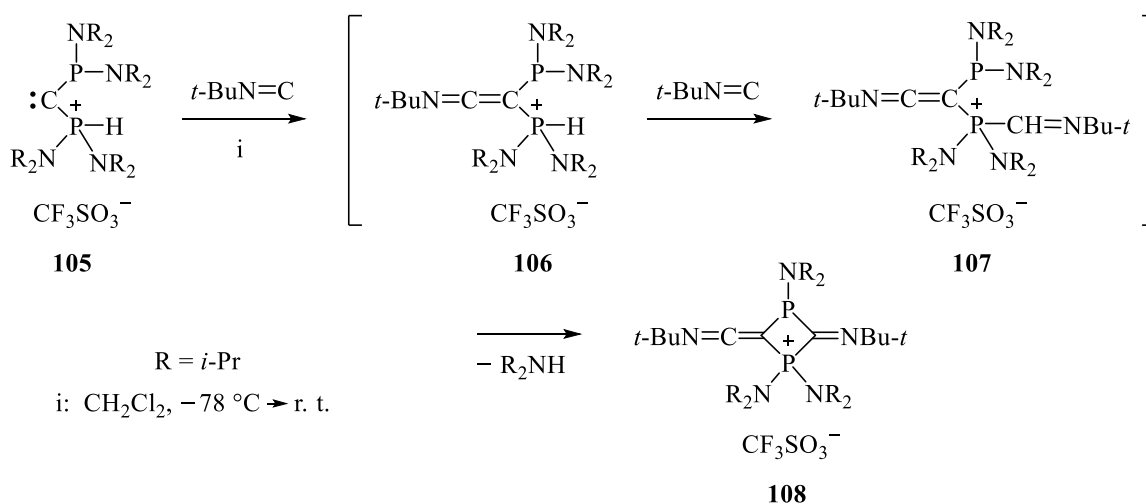
## Scheme 23

### 2.6. Miscellaneous

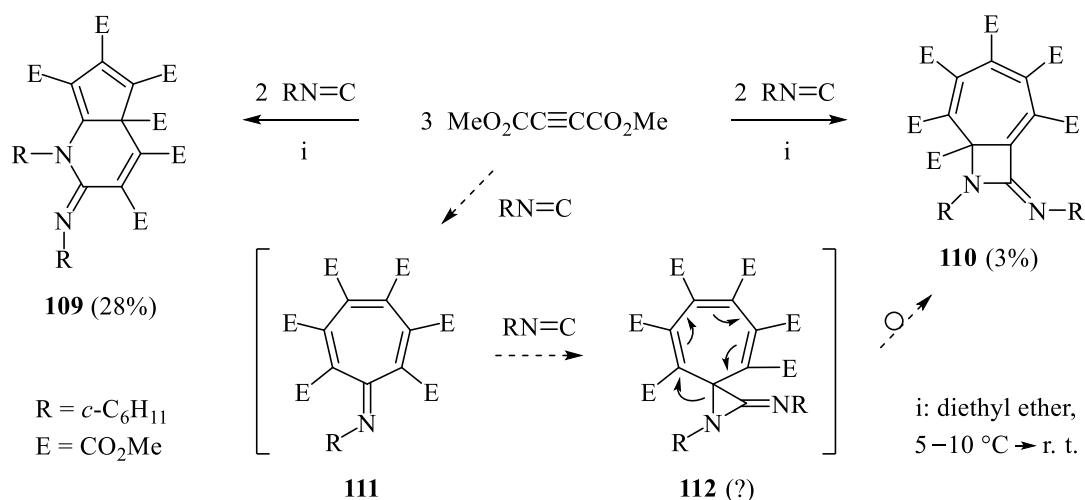
*Functionalized phosphino(phosphonio)carbene:* Treatment of the salt **105** with two equivalents of *tert*-butyl isocyanide gave rise to the 1,3-diphosphetanium ring as in **108** (no yield); employment of only one equivalent led to the recovery of 50% of the starting substrate (Scheme 24).<sup>65</sup> The reaction commenced with formation of the ketenimine **106**; but, while stable when unprotonated (*cf.* ref.<sup>66</sup>), this species rapidly inserts the second isocyanide into the P–H bond to give an intermediate like **107** which underwent ring closure through elimination of diisopropylamine.

*Butynedioic acid ester:* It is known that reactions of isocyanides with dimethyl butynedioate (DMAD) do not follow the pattern of Section 2.1, *i.e.* giving cyclobutenediimines.<sup>2</sup> However, a four-membered ring may arise from that reagent by another route. Indeed, a more recent study using cyclohexyl isocyanide has shown that – besides the cyclopenta[*b*]pyridine **109** (including minor quantities of an isomer and a 1-azaspiro[4.4]nonatriene) – the cyclohepta-anellated azetidiniimine **110** was formed (Scheme 25).<sup>67,68</sup> As a direct precursor the 3:1 cycloadduct of DMAD and the isocyanide, *i.e.* the cycloheptatrienimine **111**, has been invoked.<sup>67</sup> To rationalize its conversion into **110**, a transient species like **112** is added here tentatively. Ensuing work of other

authors concentrated on the preparation of **109** (including an X-ray study of the product); additional compounds were not reported.<sup>69</sup>

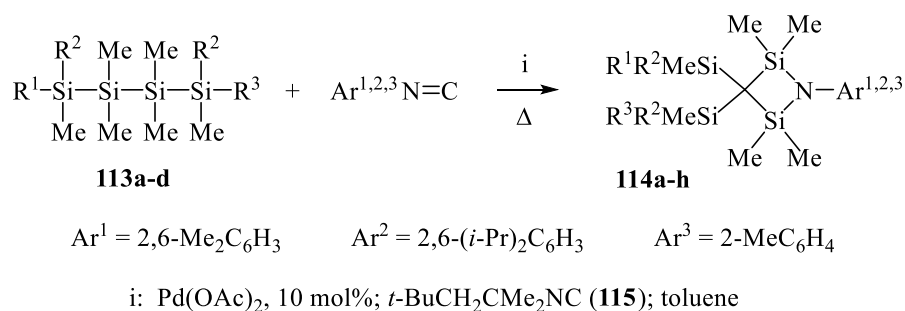


Scheme 24



Scheme 25

*Oligosilanes*: Insertion of isocyanides into the Si–Si bond involving a unique skeletal rearrangement has been encountered when the tetrasilanes **113a–c** and the hexasilane **113d** were reacted with certain aryl isocyanides in the presence of a palladium catalyst and 1,1,3,3-tetramethylbutyl isocyanide (**115**) (Scheme 26). This procedure gave the 1,2,4-azadisiletanes **114a–g** and **114h**, respectively.<sup>70,71</sup> The structures of **114c**<sup>70</sup> and **114h**<sup>71</sup> have been elucidated by X-ray crystallography. Regarding the *tert*-alkyl isocyanide **115**, this additive, without entering the four-membered ring, has proved an effective promotor in most cases as evidenced by comparison of the yields.<sup>71</sup>



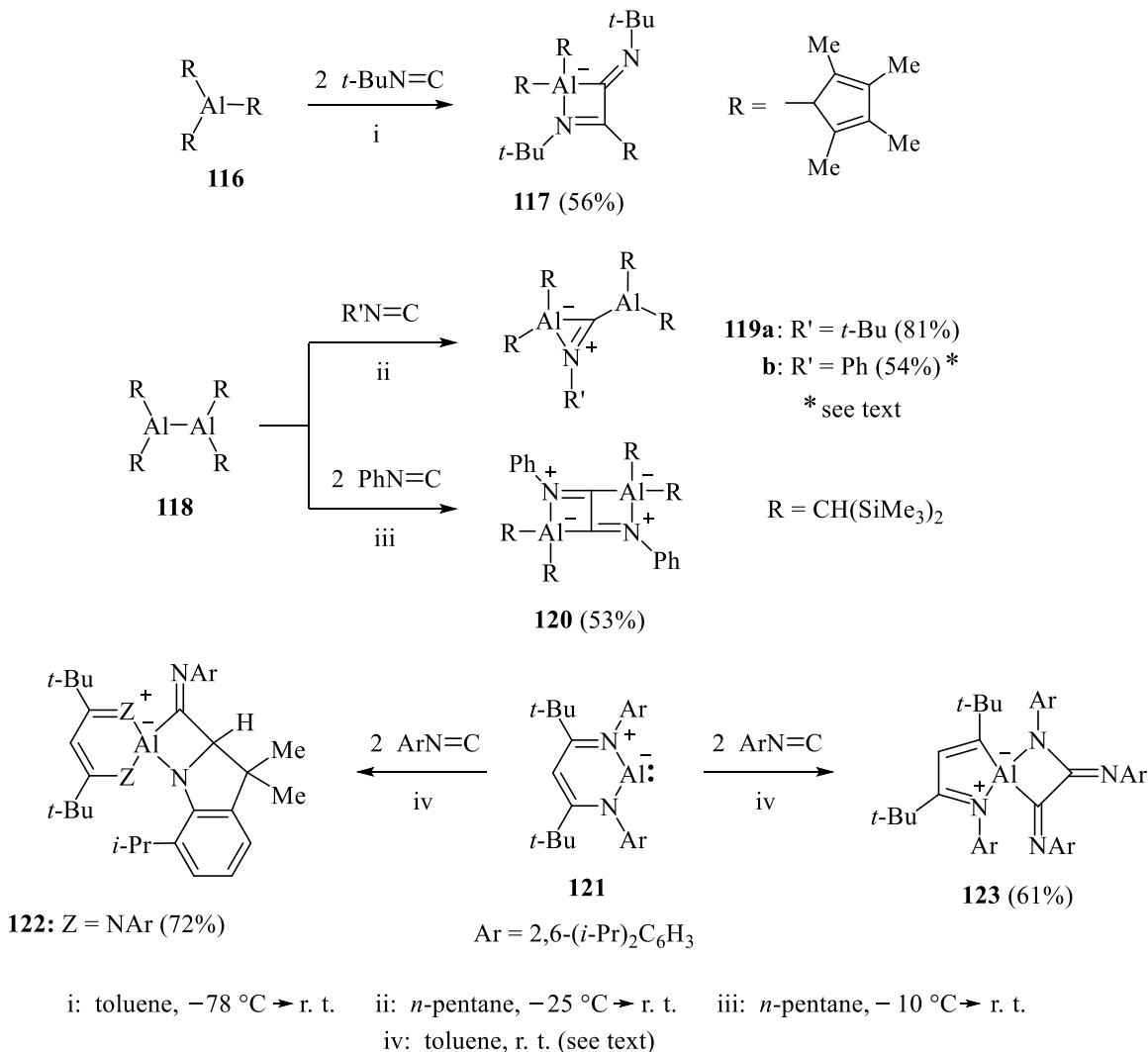
<b>113</b>	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	<b>114</b>	Yield (%) [ <b>115</b> : yes / no ]
<b>a</b>	Me	Me	Me	Ar <sup>1</sup>	40 / 9
	Me	Me	Me	Ar <sup>2</sup>	45 / 40
<b>b</b>	Ph	Me	Ph	Ar <sup>1</sup>	31 / 37
	Ph	Me	Ph	Ar <sup>2</sup>	62 / 50
	Ph	Me	Ph	Ar <sup>3</sup>	24 / 0
<b>c</b>	Ph	Ph	Ph	Ar <sup>1</sup>	28 / 10
	Ph	Ph	Ph	Ar <sup>2</sup>	48 / 54
<b>d</b>	SiMe <sub>2</sub> SiMe <sub>3</sub>	Me	Me	Ar <sup>2</sup>	15 / -

## Scheme 26

*Organoaluminum compounds:* *tert*-Butyl isocyanide was found to undergo double insertion into one Al–C bond of tris(tetramethylcyclopentadienyl)aluminum (**116**) to form the four-membered ring **117** (Scheme 27). The cyclic structure has been elucidated by X-ray diffraction. The strong Al–N linkage seems to be the driving force behind the twofold insertion which is favored to such an extent as to leave unreacted **116** when working with less than two equivalents of isocyanide.<sup>72</sup>

Insertion of isocyanides into the Al–Al bond of the dialane **118** resulted in the formation of a three- or four-membered ring, depending on the reagent and conditions. Using one equivalent of *tert*-butyl isocyanide, compound **119a** was obtained as the single product. However, phenyl isocyanide not only afforded the expected derivative **119b**, but also gave 17% of the product of double insertion, *i.e.* the bicyclic system **120**. Hence, on repeating the experiment with two equivalents of this isocyanide, compound **120** was isolated exclusively. An analogous run with *tert*-butyl isocyanide was not reported.<sup>73</sup>

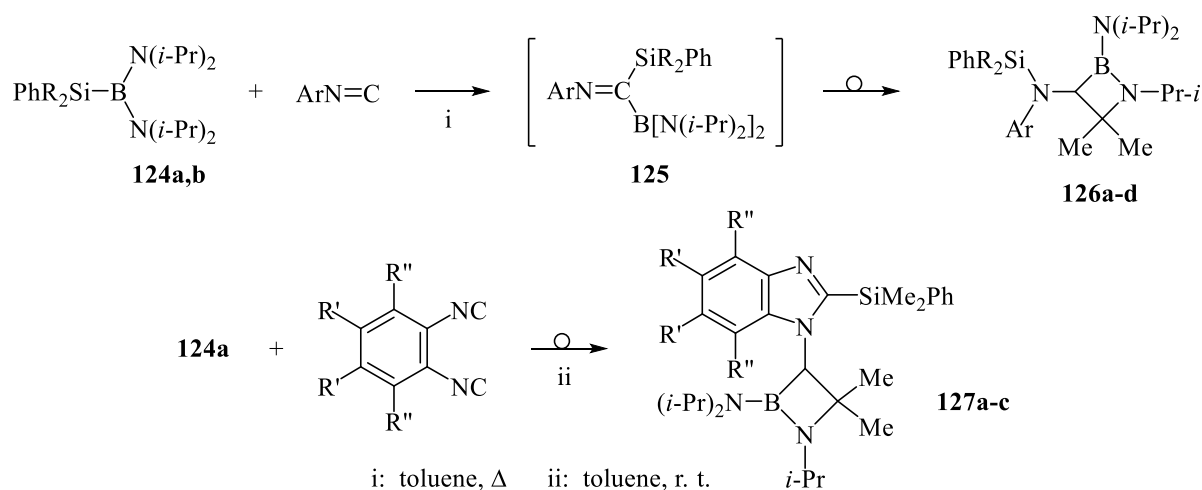
The aluminum(I) complex **121** (dealt with in this section for practical reasons) was found to react very readily with two equivalents of 2,6-diisopropylphenyl isocyanide. When this reagent was added neat to a suspension of **121** in a minimum amount of solvent, the remarkable compound **122** was isolated. Its formation was thought to proceed through consecutive coupling of both isocyanides leaving a four-membered ring, the carbenic C(4) of which interfered with the adjacent isopropyl group to give the stable product **122**. When working in a dilute medium, compound **123** arose, possibly *via* insertion of the two isocyanides into one of the Al–C bonds to be followed by a skeletal rearrangement of the resultant eight-membered ring. The structures of **122** and **123** have been determined by X-ray crystallography.<sup>74</sup>



### Scheme 27

(Diaminoboryl)silanes: Insertion of an aryl isocyanide into the Si–B bond of the borylsilanes **124** generates (boryl)(silyl)iminomethanes (**125**) (Scheme 28). Compounds of this type, *e.g.* **125a** (R = Me, Ar = 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), are obtained in high yield when working at room temperature. However, in refluxing toluene an unexpected rearrangement took place, consisting in a 1,2-shift of the silyl group to leave an (amino)(boryl)carbene species which engaged an adjacent isopropyl group to form the 1,2-azaboretidine **126a**.<sup>75</sup> The reaction was shown to be limited to isocyanides having a free *ortho*-position. Thus, while the reaction of **124a** with 2,6-dimethylphenyl isocyanide even at 110 °C did not go beyond the stage of insertion (**125**), four-membered rings like **126b-d** were formed readily from a range of 2-alkynylphenyl isocyanides. Extending the experiments to 1,2-diisocyanobenzenes, only one –N=C group reacted with the substrate to give the benzimidazolyl substituted azaboretidines **127a-c**; the two derivatives **a,b** having R'' = H were obtained at room temperature. X-ray crystallographic data are available for the products **126d** and **127a**.<sup>75</sup>

*Tris(trimethylsilyl)silyllithium*: The silyllithium substrate **128** was found to react smoothly with two molecules of 2,6-dimethylphenyl isocyanide to form, in the presence of *N,N,N',N'*-tetramethylethylenediamine (tmeda), the 1,2-dihydro-1,2-azasilole derivative **129** (Scheme 29).<sup>76</sup> The process assumedly started with the formation of a lithioaldimine followed by migration of one silyl group to generate a silene species which incorporated the second isocyanide *via* electrocyclozation. Quenching of **129** with trimethylsilyl triflate afforded the derivate **130**,<sup>76</sup> while treatment with cyclopentadiene yielded the conjugated acid **131**.<sup>77</sup> Moreover, reacting **128** in the presence of the soft 1,2-bis(dimethylphosphino)ethane gave a product **129** having THF instead of tmeda.<sup>77</sup> Detailed X-ray diffraction studies have been conducted with both **129** and **131**.<sup>76,77</sup>



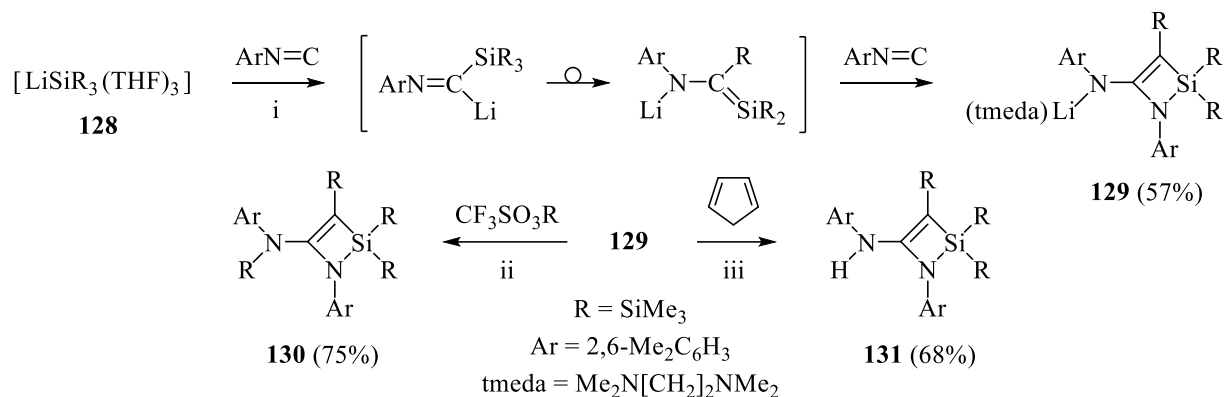
124	126	127	R	R'	R''	Ar	Yield (%)	
							126	127
<b>a</b>	<b>a</b>	<b>a</b>	Me	H	H	3,5-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	76	71 <sup>a</sup>
	<b>b</b>	<b>b</b>	Me	Me	H	2-(Me <sub>3</sub> SiC≡C)C <sub>6</sub> H <sub>4</sub>	86	54 <sup>a</sup>
	<b>c</b>	<b>c</b>	Me	H	Me	2-( <i>t</i> -BuC≡C)C <sub>6</sub> H <sub>4</sub>	82	
<b>b</b>	<b>d</b>		Ph			2-(Me <sub>3</sub> SiC≡C)C <sub>6</sub> H <sub>4</sub>	84	

<sup>a</sup> Adduct with BH<sub>3</sub>.

## Scheme 28

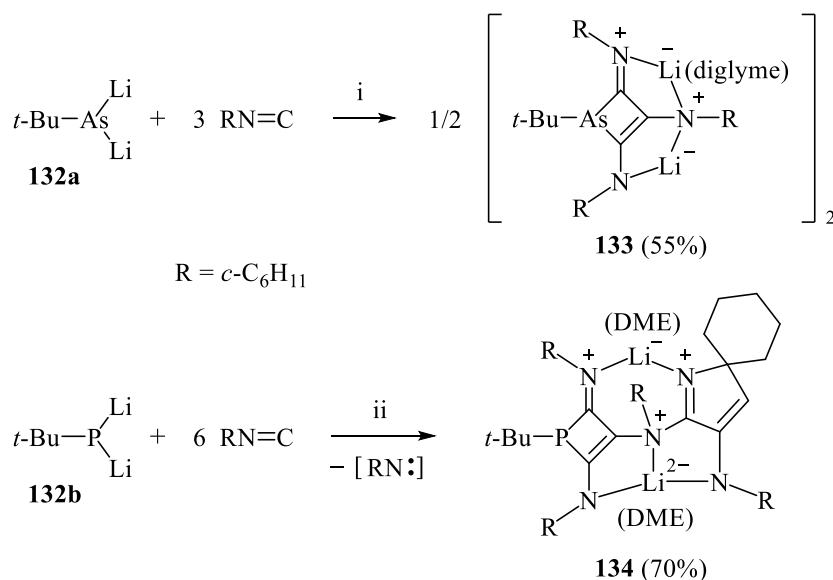
*Dilithium tert-butylarsinide and -phosphinide*: Action of the arsenic compound **132a** on cyclohexyl isocyanide caused trimerization of the latter to form the product **133** which was isolated after addition of cyclohexane and diglyme (Scheme 30). By contrast, usage of the phosphorus analog **133b** led to an engagement of six equivalents of the isocyanide to generate the more complicated structure **134** and, as a side product, an open-chain material originating from cyclohexylnitrene. The constitution of both cyclic products has been established by X-ray analyses.<sup>78</sup>





i: pentane, tmeda,  $-80^\circ C \rightarrow r. t.$  ii: pentane,  $-40^\circ C \rightarrow r. t.$  iii: pentane,  $-60^\circ C \rightarrow r. t.$

### Scheme 29



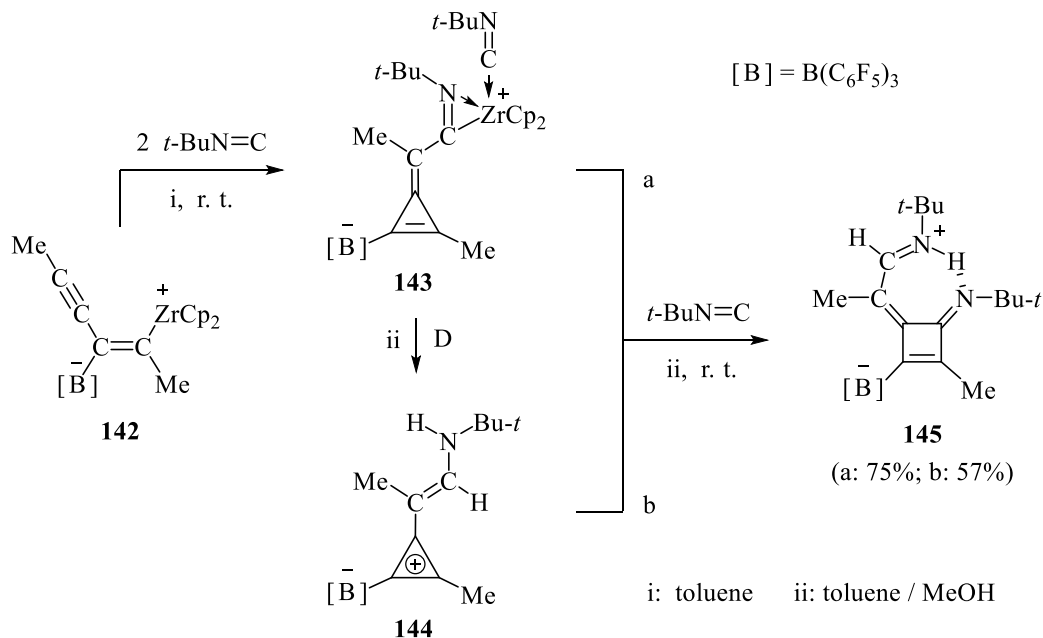
i: THF,  $20^\circ C$ ; then diglyme/*c*-hexane ii: THF,  $20^\circ C$ ; then DME

### Scheme 30

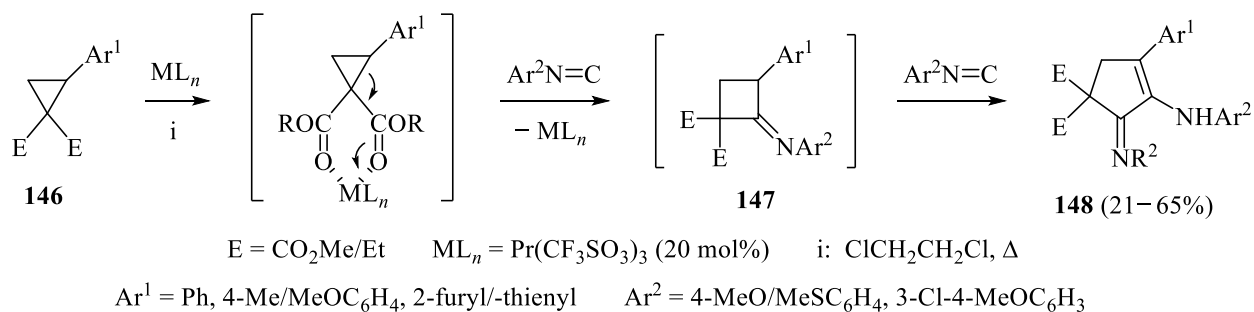
*Tetragermabutadiene*: Studies on the behavior towards the heavy chalcogens selenium and tellurium have revealed that the title substrate **135** (Scheme 31) is capable of undergoing [1+4] cycloadditions or Ge–Ge bond scissions, depending on the reagents. The former mode was followed by selenium, whereas treatment with tellurium caused fragmentation of the substrate. In this context the reaction with 2-methoxyphenyl isocyanide was probed too, showing that one Ge–Ge bond was broken: while the extruded germylene dimerized, the residual Ge<sub>3</sub> chain cyclized to the 1,4-dihydrotrigermet-4-imine **136** which was characterized by X-ray crystallography.<sup>79</sup>





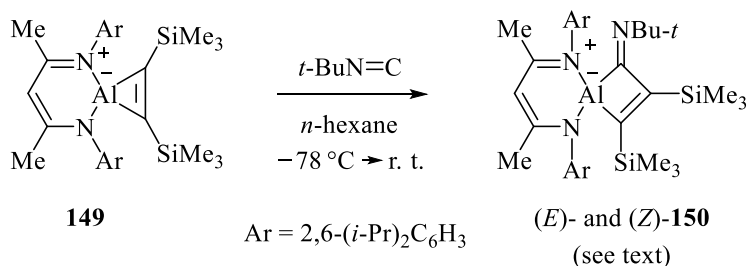


## Scheme 33



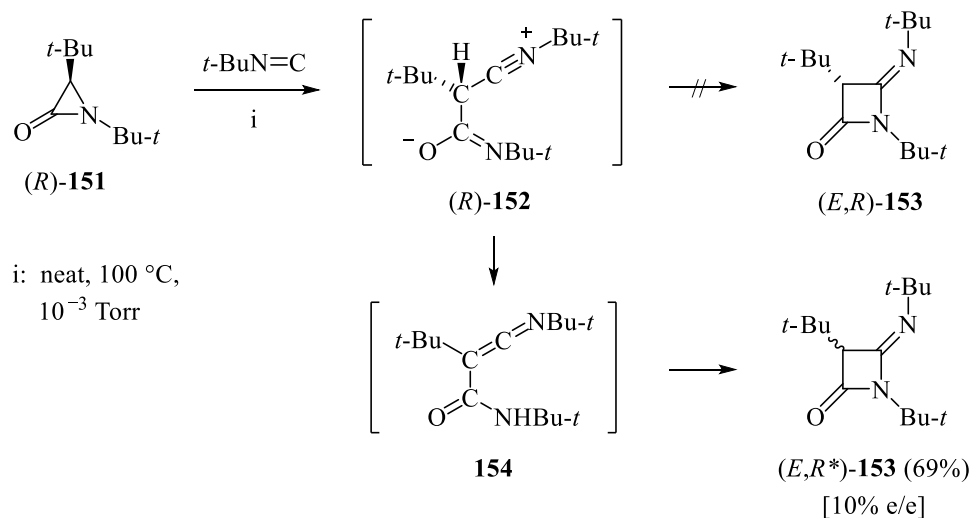
## Scheme 34

*IH-Aluminirene*: *tert*-Butyl isocyanide was found to insert under very mild conditions into the aluminirene unit of the spiro substrate **149** to form the unique molecule **150**. Of this compound stable *E* and *Z* isomers were detected by NMR spectroscopy. Crystallization gave a solid in 57% yield that, according to X-ray diffraction, represented the *Z* configured form. It may be added by analogy that carbon monoxide transformed **149** into the corresponding aluminetimine.<sup>86</sup>



### Scheme 35

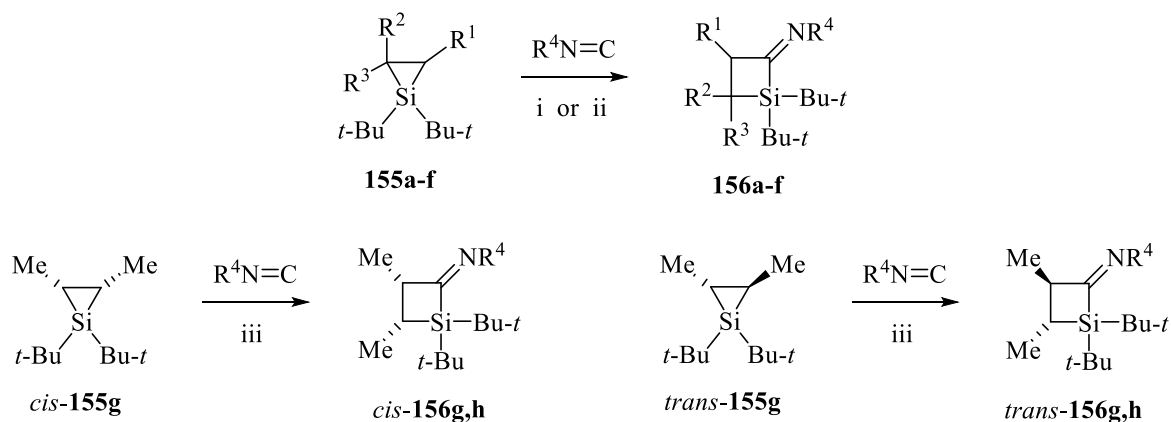
*$\alpha$ -Lactams:* The conversion of this class into imino-substituted  $\beta$ -lactams through reaction with isocyanides is well established.<sup>2</sup> In a more recent work a stereochemical aspect was investigated (Scheme 36).<sup>87</sup> Heating the enantiomer (*R*)-**151** with *tert*-butyl isocyanide gave rise to a  $\beta$ -lactam like (*E,R*\*)-**153** of unknown absolute configuration (low enantiomeric excess), *i.e.* the stereochemical information got almost lost (if not fully). This was rationalized by considering the behavior of the zwitterionic intermediate (*R*)-**152**: this species, formed with inversion at C(3), did not cyclize directly [which must have led to (*E,R*)-**153**], but in a competing step it underwent a 1/→3/hydrogen shift to generate the ketenimine **154** which would yield racemic (*E*)-**153**.




### Scheme 36

*Siliranes:* The insertion of isocyanides into siliranes was found to affect the Si–C bond. The first known examples originated from experiments with substrates like **155a-c** and aryl isocyanides which gave the siletan-2-imines **156a-c** (Scheme 37). Of these products the derivative **156b** has been studied by X-ray diffraction, showing a practically planar four-membered ring with elongated Si–C and C–C bonds and a *Z* configured imine function.<sup>88</sup> Soon thereafter other authors<sup>89</sup> investigated regioselectivity and stereospecificity: (i) Studying the behavior of the monosubstituted

siliranes **155d-f** towards *tert*-butyl isocyanide, they found that insertion occurred at the more substituted Si–C bond ( $\rightarrow$  **156d-f**), but this regioselectivity was gradually eroded as the substituent R<sup>1</sup> became bulkier. (ii) Reactions of *cis*- and *trans*-**155g** with *p*-tolyl and *tert*-butyl isocyanide revealed that the formation of the respective siletan-2-imines **156g,h** proceeded with stereospecific retention of configuration. As for the reactivity of these compounds, it was observed *inter alia* that both *cis*- and *trans*-**156g,h** tautomerize to 2-amino-1,4-dihydrosiloles on heating.<sup>89</sup>



i: r. t. (solvent unreported) (for **a-c**)    ii: benzene,  $\Delta$  (for **d-f**)    iii: benzene, r. t. (for **g**) or  $\Delta$  (for **h**)

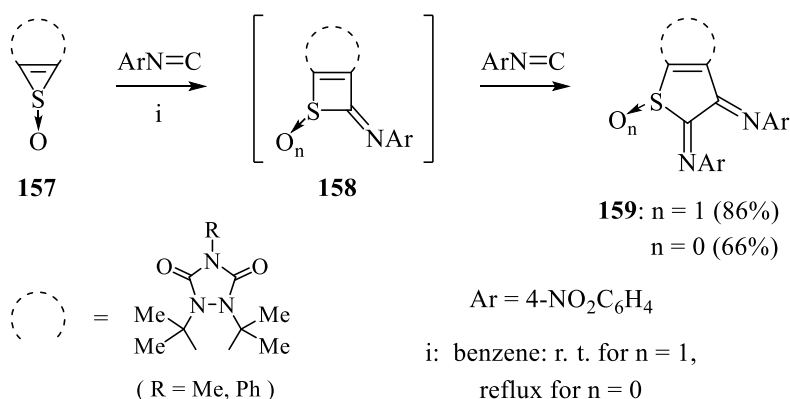
<b>155, 156</b>	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	Yield (%)	Regioselectivity <sup>b</sup>
<b>a</b>	H	Me	Me	Ph	55	
<b>b</b>			H	Ph	42	
<b>c</b>	–[CH <sub>2</sub> ] <sub>3</sub> –		H	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	34	
<b>d</b>	<i>n</i> -Bu	H	H	<i>t</i> -Bu	94 <sup>a</sup>	> 95 / 5
<b>e</b>	<i>i</i> -Pr	H	H	<i>t</i> -Bu	98 <sup>a</sup>	92 / 8
<b>f</b>	<i>t</i> -Bu	H	H	<i>t</i> -Bu	97 <sup>a</sup>	86 / 14
<i>cis</i> - <b>g</b> <sup>c</sup>				4-MeC <sub>6</sub> H <sub>4</sub>	96	
<i>trans</i> - <b>g</b> <sup>c</sup>				4-MeC <sub>6</sub> H <sub>4</sub>	86	
<i>cis</i> - <b>h</b> <sup>c</sup>				<i>t</i> -Bu	99	
<i>trans</i> - <b>h</b> <sup>c</sup>				<i>t</i> -Bu	98	

<sup>a</sup> Yields refer to isolated products. <sup>b</sup> By <sup>1</sup>H NMR spectroscopy. <sup>c</sup> One diastereoisomer by <sup>1</sup>H NMR spectroscopy.

### Scheme 37

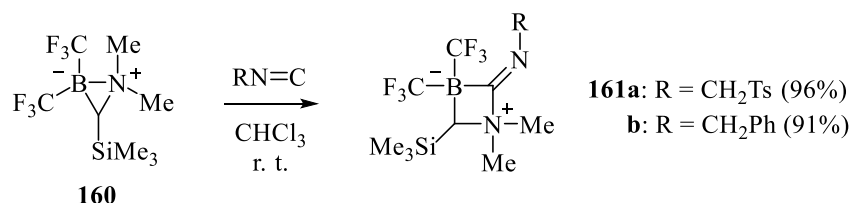
*Thiirene S-oxides*: Isocyanide insertion into the thiirene half-ring of **157** has been accomplished with 4-nitrophenyl isocyanide (Scheme 38).<sup>90</sup> However, as observed with the cyclopropane derivative **146** (*cf.* Scheme 34), the reaction did not stop at the four-membered ring (**158**), but proceeded with double insertion to give a thiophenediimine **159** which, depending on the conditions,

was obtained as *S*-oxide ( $n = 1$ ) or deoxygenated ( $n = 0$ ). Since four equivalents of the isocyanide were applied in both experiments, it is open whether **158** constitutes an elusive species.



### Scheme 38

*Azoniaboranuidacyclopropane*: The title substrate **160** was found to react readily with tosyl and benzyl isocyanide to give in excellent yield the 1-azonia-3-boranuidacyclobutanimes **161a** and **b**, respectively (Scheme 39). The structure of **161a** has been elucidated by X-ray diffraction.<sup>91</sup>



### Scheme 39

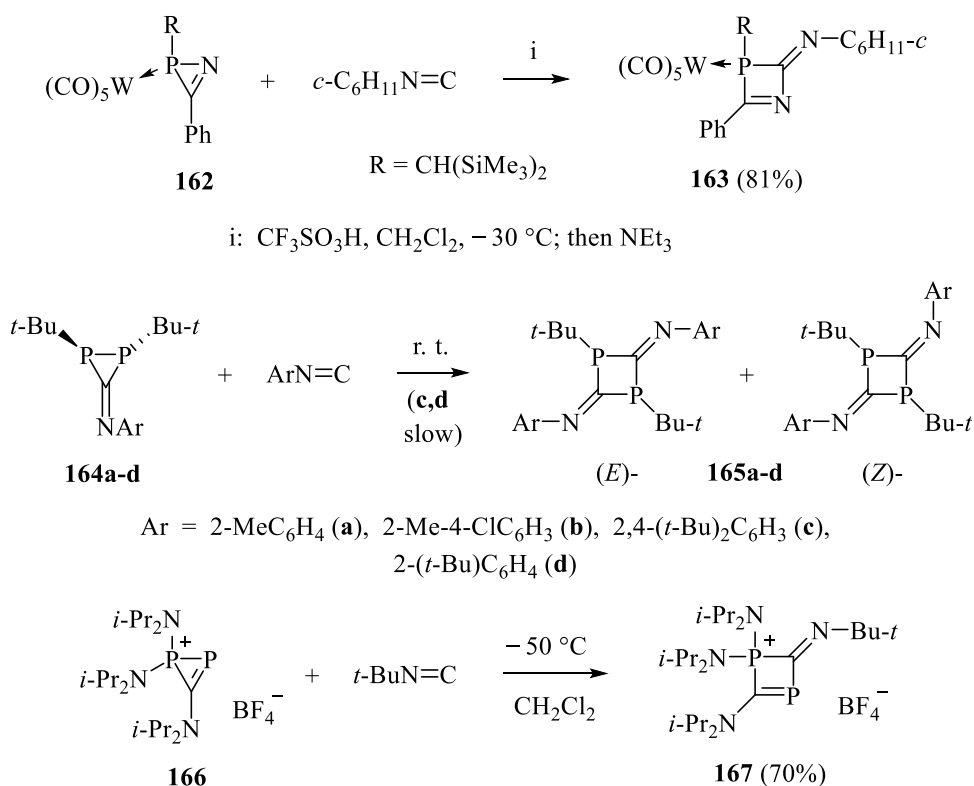
*Azasiliridines*: For preparative reasons this class of compounds is dealt with in Section 2.2.

*2H-Azaphosphirene*: In the presence of a stoichiometric amount of triflic acid the azaphosphirene complex **162** underwent rapid insertion of cyclohexyl isocyanide (Scheme 40). When the reaction was quenched with triethylamine after five minutes, the dihydro-1,3-azaphosphete complex **163** was obtained in high yield. Its structural parameters have been determined by the X-ray method. Interestingly, the 3-(2-thienyl)-substituted analog of **162** did not form the corresponding product **163** (2-thienyl instead of Ph), but was converted into a *2H*-azaphosphole derivative.<sup>92</sup>

*Diphosphiranes, diphosphirenium*: The insertion of isocyanides into the P–P bond of diphosphiranes appears as a consequence of decomposition rather than representing a preparative concept (Scheme 40).<sup>93</sup> Substrates like **164a-d** (made from isocyanide dichlorides and alkali diphosph-

ides) proved partially labile, depending on the Ar substituent: The derivatives **a** and **b** having sterically less demanding ligands released isocyanide within a few hours that reacted with residual **164a,b** to give mixtures of the *E*- and *Z*-configured 1,3-diphosphetane-2,4-diimines **165a,b**; in the case of the derivatives **164c,d**, the bulkier substituents caused the respective conversion ( $\rightarrow$  **165c,d**) to occur much more slowly.<sup>93</sup>

Another example of P–P bond breaking by an isocyanide was observed on treatment of the diphosphirenium salt **166** with *tert*-butyl isocyanide. As the product of insertion the 1,2-dihydro-1,3-diphosphetium derivative **167** resulted, which was characterized also by X-ray diffraction.<sup>94</sup>



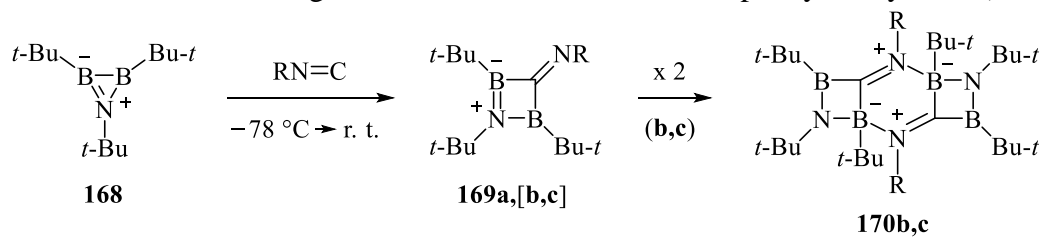
#### Scheme 40

*Azadiboriridine*: Isocyanides were found capable of breaking the B–B bond of the azadiboridine **168** (Scheme 41). The nature of the products depends on the R ligand of the reagent: Usage of the sterically demanding 2,6-dimethylphenyl isocyanide (one equivalent only!) gave rise to the 1,2,4-azadiboretidin-3-imine **169a**, whereas the analogous products from methyl and ethyl isocyanide, *i.e.* **169b,c**, eluded isolation by undergoing a [3+3] cyclodimerization which led to the tricycles **170b,c**. Of these derivatives, **170b** has been submitted to an X-ray diffraction study.<sup>95</sup>

*Trisilirane, trigermirane*: Three-membered cycles having silicon or germanium as the sole ring atoms readily incorporate isocyanides (Scheme 42). Thus, on heating **171** with an aryl isocyanide

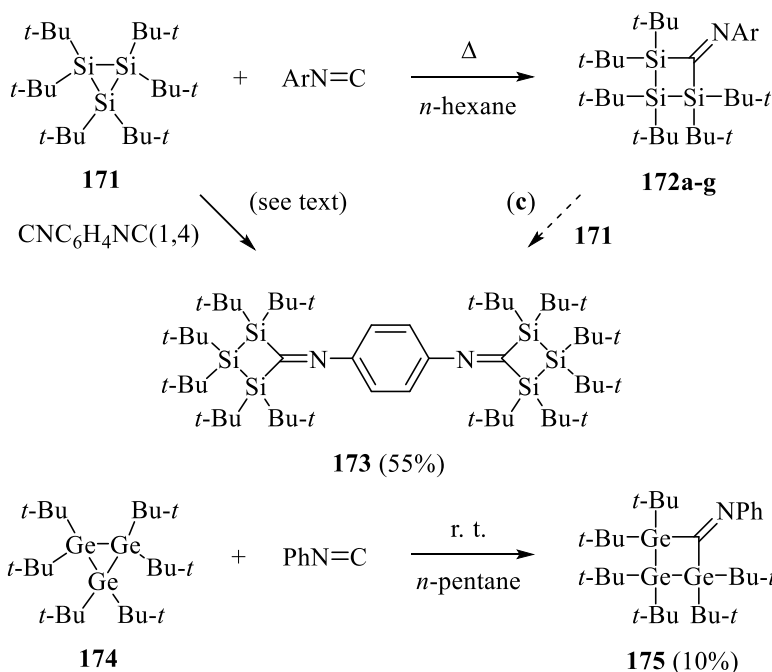


the trisiletanimines **172a-d**<sup>96</sup> and **172e-g**<sup>97</sup> were formed. Regarding 1,4-diisocyanobenzene, less than one equivalent led to the 'bis' derivative **173** which is also accessible stepwise *via* **172c**; this product<sup>96</sup> as well as compound **172f**<sup>97</sup> has been studied by X-ray diffraction. The same kind of conversion occurred with the trigermirane **174** when treated with phenyl isocyanide ( $\rightarrow$  **175**).<sup>98</sup>



<b>169, 170</b>	R	solvent	Yield (%)
<b>a</b>	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	61 ( <b>169a</b> )
<b>b</b>	Me	pentane	89 ( <b>170b</b> )
<b>c</b>	Et	hexane	92 ( <b>170c</b> )

## Scheme 41

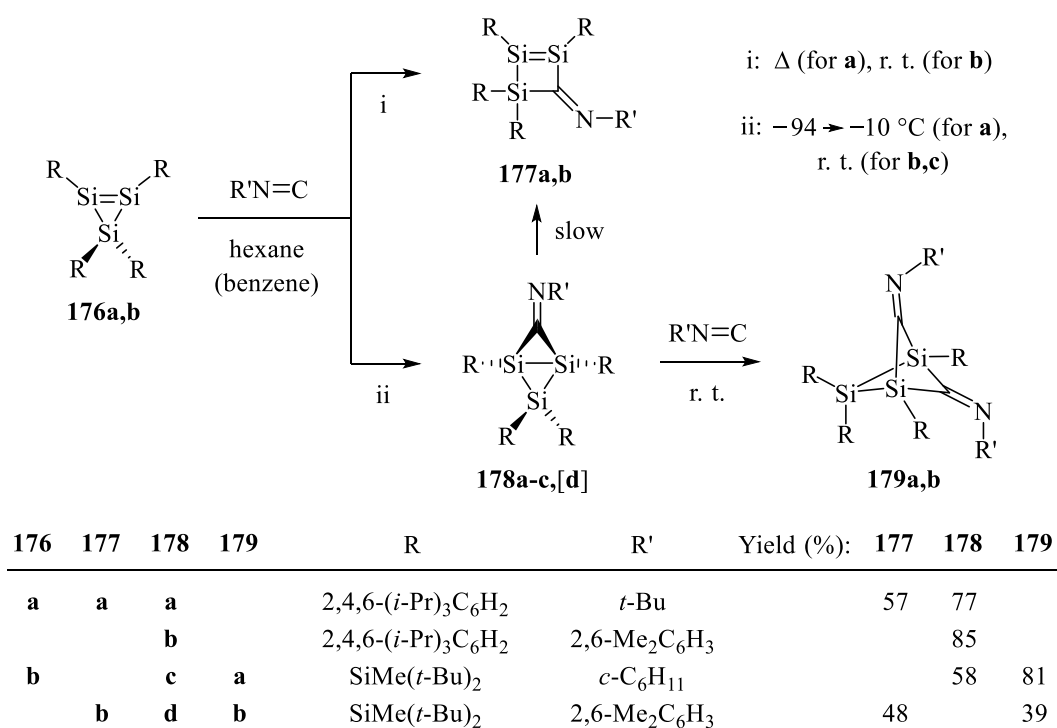


<b>172</b>	Ar	Yield (%)	<b>172</b>	Ar	Yield (%)
<b>a</b>	Ph	75	<b>e</b>	2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	18
<b>b</b>	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	68	<b>f</b>	2,6-( <i>i</i> -Pr) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	30
<b>c</b>	4-CNC <sub>6</sub> H <sub>4</sub>	61	<b>g</b>	1-naphthyl	78
<b>d</b>	2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	46			

## Scheme 42

*Trisilirenes*: The behavior of this class of compounds towards isocyanides is characterized by two competing reaction modes, *i.e.* insertion into the three-membered ring and [1+2] cycloaddition across the double bond.<sup>99</sup> Starting from the substrates **176a,b**, the trisiletimines **177a,b** and the trisilabicyclo[1.1.1]butanes **178a-c** were prepared (Scheme 43). According to a DFT study on the models **177** and **178** having R = SiMe<sub>3</sub> / R' = *c*-C<sub>6</sub>H<sub>11</sub> and 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, the derivatives **178** were found higher in energy by 2.4 and 5.1 kcal/mol, showing that they arise under kinetic control. This is best demonstrated by the reaction of **176a** with *tert*-butyl isocyanide: At room temperature a mixture of **177a** and **178a** was formed immediately; on standing, the latter component slowly rearranged to **177a**; yet, working at -94 °C, only compound **178a** was observed. – X-ray diffraction studies have been performed with **177a,b** and **178b,c** (**b**: adduct with hexane).<sup>99</sup>

In certain cases the isocyanide opened the Si–Si bridge in **178** to give a trisilabicyclo[1.1.1]pentane **179**. This occurred on prolonged treatment of **176b** with two equivalents of cyclohexyl isocyanide (→ **179a**); using 2,6-dimethylphenyl isocyanide, the formation of **179b** took place even in five minutes, the intermediate **178d** being undetectable.<sup>99</sup>

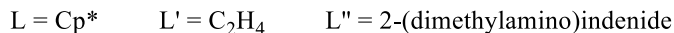
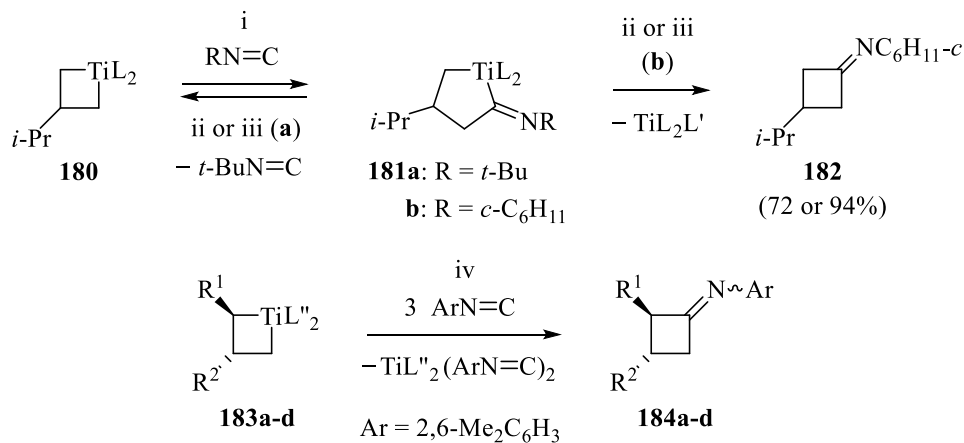


Scheme 43

### 3.2. Migratory insertion of isocyanides into metallacycles

*Titanacyclobutanes*: A synthetically useful synthesis of cyclobutananimines has been developed by starting from the titanacycles **180** and **183a-d** (Scheme 44).<sup>100</sup> Treatment of compound **180** with

*tert*-butyl and cyclohexyl isocyanide gave, respectively, the titanacyclopentanimines **181a** and **b** in  $\geq 90\%$  yield. Moderate heating of the latter induced ring contraction with demetalation to afford the cyclobutanimine **182** in 72% yield (or 94% when working in the presence of ethene).

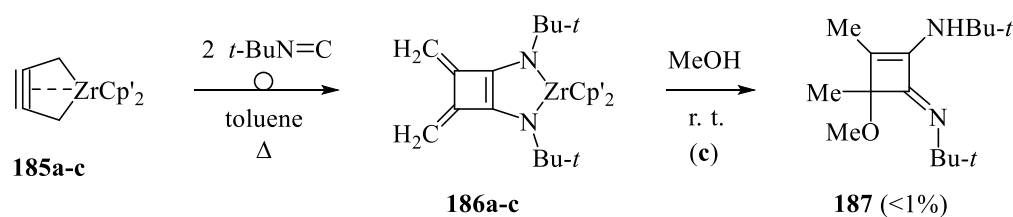


i: toluene,  $-78\text{ }^\circ\text{C} \rightarrow \text{r. t.}$     ii: toluene,  $65\text{ }^\circ\text{C}$     iii: C<sub>2</sub>H<sub>4</sub> (10 psi), toluene,  $65\text{ }^\circ\text{C}$   
 iv: THF,  $-35\text{ }^\circ\text{C} \rightarrow \text{r. t.}$

<b>183, 184</b>	R <sup>1</sup>	R <sup>2</sup>	Yield (%)	<i>E</i> : <i>Z</i> ratio
<b>a</b>	Me	CH <sub>2</sub> Ph	quant	6 : 1
<b>b</b>	Me	<i>i</i> -Pr	90	>99 : <1
<b>c</b>	Ph	CH <sub>2</sub> Ph	quant	6 : 1
<b>d</b>	Ph	<i>i</i> -Pr	86	10 : 1

#### Scheme 44

The *tert*-butyl analog **181a**, however, reverted to the starting ring **180** when submitted to either procedure. In a second series of experiments the authors reacted the disubstituted (*trans*-configured) substrates **183a-d** with a threefold excess of 2,6-dimethylphenyl isocyanide. Here the intermediary five-membered rings were not isolated, but in a stereocontrolled manner directly converted into the cyclobutanimines **184a-d**.<sup>100</sup>



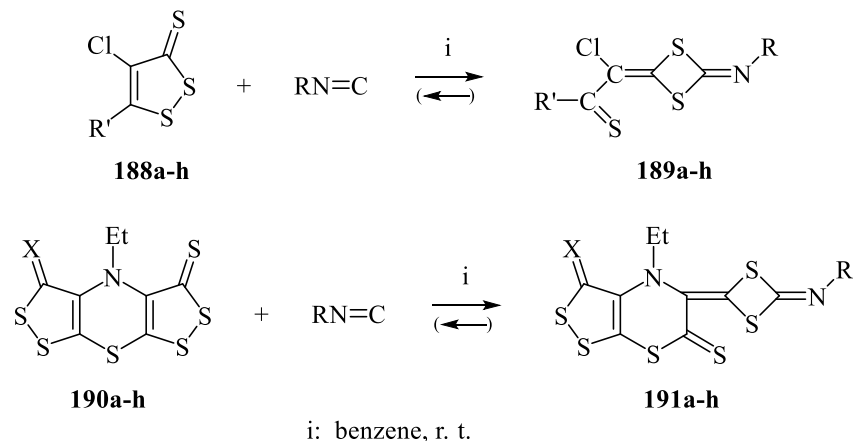
<b>185, 186</b>	<b>Cp'<sub>2</sub></b>	<b>Yield (%)</b>
<b>a</b>	Cp <sub>2</sub>	85
<b>b</b>	[η <sup>5</sup> -( <i>t</i> -Bu)C <sub>5</sub> H <sub>4</sub> ] <sub>2</sub>	44
<b>c</b>	Me <sub>2</sub> Si(η <sup>5</sup> -C <sub>5</sub> H <sub>4</sub> ) <sub>2</sub>	56

### Scheme 45

*1-Zirconacyclopent-3-yne*: Another, rather unexpected migratory insertion of an isocyanide was observed with the zirconacycles **185a-c** (Scheme 45). At slightly elevated temperature two equivalents of *tert*-butyl isocyanide were inserted into the β-Zr–C bonds, followed by a skeletal rearrangement to form the bicyclic compounds **186a-c** with a four-membered half-ring. Methanolysis of the derivative **186c** gave the monocycle **187** which, like the products **186b,c**, was studied by X-ray crystallography.<sup>101</sup> – The mechanism was the subject of extensive speculations, among which the assumption of an equilibrium between structure **185** and the isomeric butatriene complex placed the reaction into the neighborhood of the process **4** → **5** shown in Scheme 1.<sup>101</sup>

### 3.3. Ring transformations

*3H-1,2-Dithiole-3-thiones*: Under mild conditions dithiolethiones like **188a-h** were transformed into the 1,3-dithietan-2-imines **189a-h** on treatment with the respective isocyanides (Scheme 46). The reaction was shown to be reversible, especially at elevated temperature. Studying the scope, the authors found that substrates **188** lacking electron-withdrawing substituents were unreactive, nor did a reagent like benzyl isocyanide enter the process.<sup>102</sup> The same kind of reaction occurred with the fused systems **190a-h** to give the derivatives **191a-h**.<sup>102,103</sup> These examples demonstrate that a dithiolone moiety (as present in **190a-e**) is not affected and, second, that in the case of the bis(thioxodithiolo) fused thiazines **190f-h** only one of the two five-membered anellands will be involved. Moreover, replacement of the central thiazine ring in **190** with a 6π cycle like pyrrole (which on ring transformation would lose its aromaticity) resulted in total loss of reactivity.<sup>102</sup>

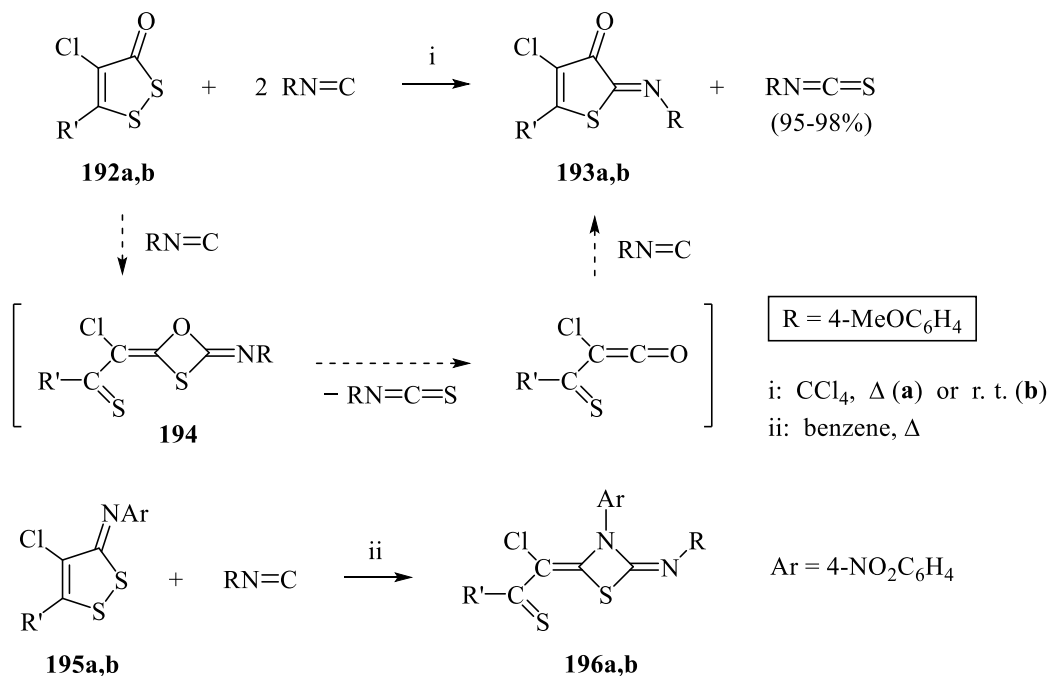


<b>188, 189</b>	R'	R	Yield (%)	<b>190, 191</b>	X	R	Yield (%)
<b>a / e</b>	Cl / SPh	CH <sub>2</sub> Ts	92 / 84	<b>a / f</b>	O / S	CH <sub>2</sub> Ts	64 / 61
<b>b / f</b>	Cl / SPh	Ph	72 / 73	<b>b / g</b>	O / S	Ph	38 / 42
<b>c / g</b>	Cl / SPh	4-MeOC <sub>6</sub> H <sub>4</sub>	72 / 68	<b>c</b>	O	4-MeOC <sub>6</sub> H <sub>4</sub>	74
<b>d / h</b>	Cl / SPh	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	85 / 84	<b>d</b>	O	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	77
				<b>e / h</b>	O / S	CH <sub>2</sub> CO <sub>2</sub> Et	41 / 39

### Scheme 46

*3H-1,2-Dithiol-3-ones*, *-3-imines*: Modifying the above conditions, it was found that also the hitherto unreactive 3-oxo-substituted 1,2-dithiole moiety is convertible. Experiments with both fused and monocyclic substrates revealed that a 1:2 reaction occurred to give a thiophene derivative besides an isothiocyanate, as illustrated by the process **192a,b** → **193a,b** (Scheme 47).<sup>104,105</sup> To rationalize this finding, the authors invoked a transient 1,3-oxathietane (**194**) which *via* [2+2] cycloreversion generates an  $\alpha$ -thioxoketene that is ring-closed by the second isocyanide.<sup>104</sup>

Quite different from substrates of the type **192**, imino congeners like **195a,b** yielded isolable four-membered rings (**196a,b**) when heated with the same isocyanide.<sup>106</sup>

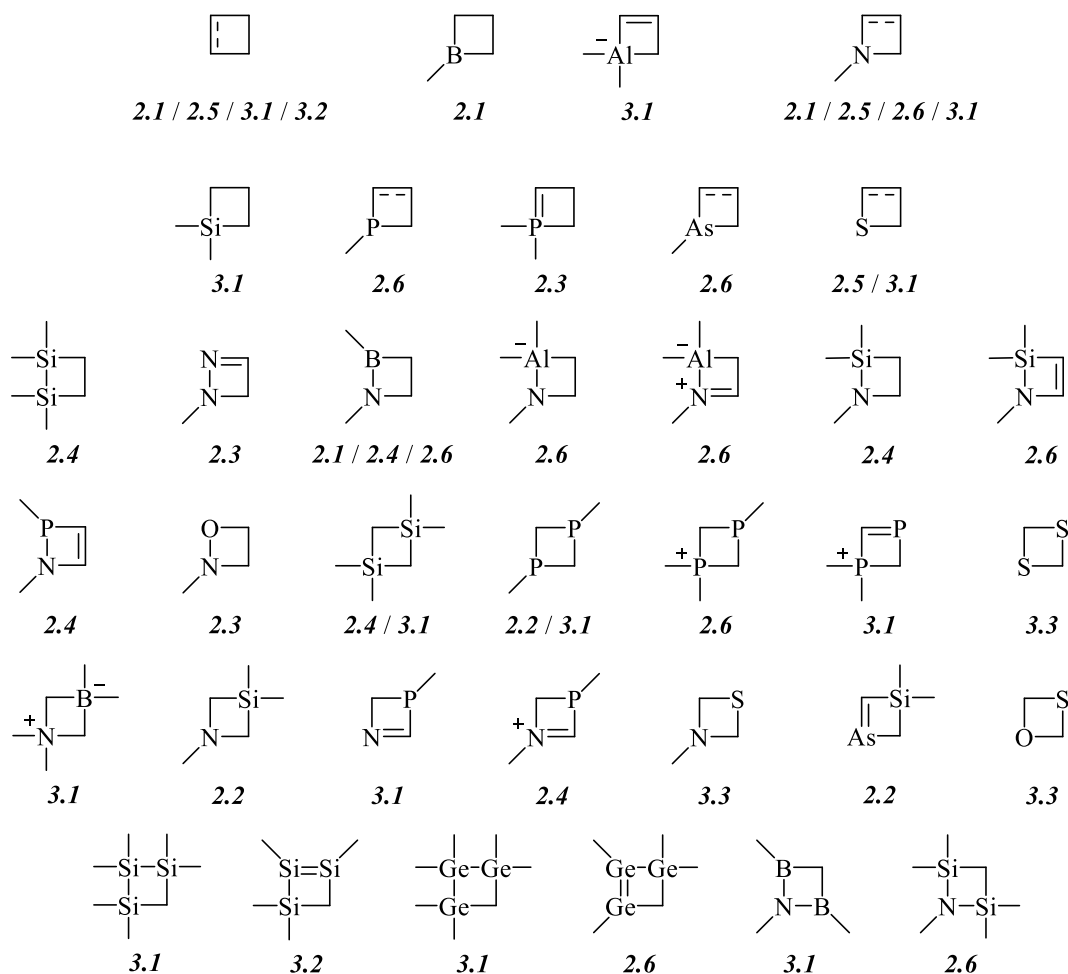


192, 193	R'	Yield (%)	195, 196	R'	Yield (%)
<b>a</b>	SPh	73	<b>a</b>	Cl	43
<b>b</b>	morpholino	54	<b>b</b>	PhO	47

### Scheme 47

## 4. Conclusions

In the preceding pages we have tried to demonstrate the growing importance of isocyanides for the construction of four-membered rings. Meanwhile their diversity has gained an imposing width, as summarized below (Chart 1). Quite a number of these rings are formed with exceptional ease and are difficult to obtain by other methods. Yet, the synthetic potential of several reactions has not been fully exploited; certain transformations wait for mechanistic studies. An additional target might be the cyclic tetramerization of isocyanides to give tetraaza[4]radialenes – a pattern that is formally present in the 'four-over-one' helix (4<sub>1</sub>) of poly(isocyanides).<sup>107</sup>



**Chart 1.** Ring systems from isocyanides (numerals indicate relevant sections).

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### Author's Biography



Dietrich Moderhack, born 1940 in Berlin, graduated from Technical University Braunschweig, Germany, where he took his PhD in 1968 (mentor: Prof. G. Zinner). From October 1974 to September 1975 he held a DFG scholarship for joining Prof. Katritzky's group at the University of East Anglia in Norwich, UK. After his Habilitation in Braunschweig (1978), he became a full Professor (1982); since October 2005, he has been retired. His major interests include triazole and tetrazole chemistry, but azapentalenes, four-membered rings with two adjacent heteroatoms and isocyanides are being looked at as well.