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Review

2,3-Dihydroimidazol-2-ylidenes and their main group element chemistry

Norbert Kuhn*, Ahmed Al-Sheikh

Institut für Anorganische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

Dedicated to Professor Ekkehard Lindner on the occasion of his 70th birthday.

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Contents

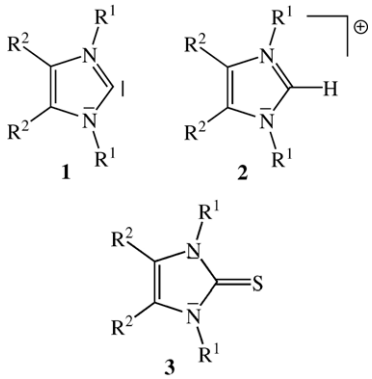
Abstract

The coordination chemistry of stable or in situ accessible carbenes is still rapidly developing. Owing to their strong basicity, they may act both as ligands in coordination compounds and as bases or reducing agents. This report reviews the reactions of 2,3-dihydroimidazol-2-ylidenes with main group element compounds and the reactions of the resultant products. A list of compounds including information about synthesis and instrumental analysis is given at the end of the report.

Keywords: Carbenes; Heterocycles; Main group elements; Carbene complexes

1. Introduction

There has been much interest in 2,3-dihydroimidazol-2-ylidene carbenes (**1**) [1] since the pioneering work of Wanzlick [2] and Arduengo [3]. The deprotonation of imidazolium ions **2** [3] and reduction of the corresponding thiones **3** with potassium metal [4] opened up convenient routes for their synthesis, and further investigation.



* Corresponding author. Tel.: +49 7071 29 76218; fax: +49 7071 29 5224.
E-mail address: norbert.kuhn@uni-tuebingen.de (N. Kuhn).

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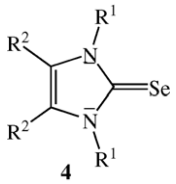

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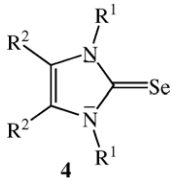
Owing to their highly nucleophilic character, heterocyclic carbenes **1** act as ligands in complexes of metal and metalloid centres in a similar manner to tertiary phosphanes. There is special interest in carbene complexes as part of catalytic cycles, and the extensive chemistry of their transition metal complexes has been reviewed separately [5]. Thiones (**3**), selones (**4**) and their benzimidazole derivatives are commonly prepared by routes not involving carbenes. Their chemistry has been extensively investigated, especially reactions involving halogens and pseudohalogens, and has been reviewed elsewhere [6]. In addition, a comprehensive overview focussing on the chemistry of basic imine (**5**) and methylene (**6**) derivatives has been previously presented [7,8].



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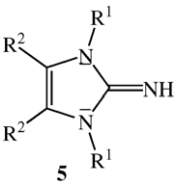

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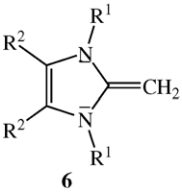

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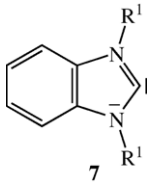
This review describes reactions of derivatives of **1** and **7** with Lewis-acidic reactants, and the chemistry of the compounds formed. A list of compounds of types **8** and **9** (E being linked to the carbene by a main group element) will be given at the end of the report. The chemistry of tetrahydroimidazol-2-ylidenes (**10**) is not part of this review.



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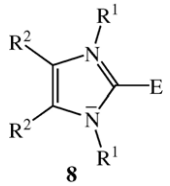

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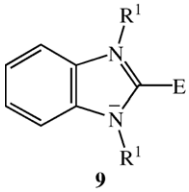

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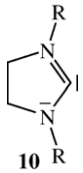

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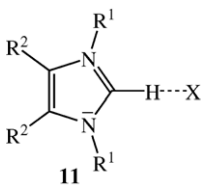
2. Reactions with hydrogen compounds

As a result of the strongly basic character of heterocyclic carbenes **1** [9], they react with *Broenstedt* acids and have consequently been used as selective deprotonation reagents. The 2H-imidazolium salts **2** [10] formed by this method are accessible by other routes; alkylation of 2H-imidazoles [11], cyclization reactions [12] or from the thiones and nitric acid [13]), and may be used as precursors in the synthesis of **1** through deprotonation [3,14]. The reaction of the carbenes with the corresponding ammonium salts gives interesting results [15]. The reaction of **1** with deuterated solvents starting with the deuteration at C2 has been discussed [16]. In the solid state, a couple of salts containing ion pairs [17] linked by hydrogen bonds (**11**) have been characterised by structural analysis (e.g. X = HF_2 [18], Cl [3,12,19–24], Br [28,29], I [28,29,31–33], ClO_4 [34], 1/2 SO_4 [35], 1/2 S_2O_7 [36], CF_3SO_3 [37], NO_2 [35], NO_3 [35], PF_6 [38,39], cyclopentadienide [40], fluorenide [41], *N*,*N*′-diphenylureate [42], $C_6H_6BrO_4$ [43], TCNQ [44,45], BF_4 [46,47], $B(OMe)_4$ [48], BR_4 [49–51], hydroborates [52], $AlBr_4$ [28,29], Ga_2I_5 [53], $InBr_4$ [54], (Carb)$InCl_4$ [55], (Carb)$InBr_4$ [55], Cp_2YbCl_2 [40], 1/2 $CoCl_4$ [56], 1/2 $NiCl_4$ [56], 1/2 $PdCl_4$ [57,58], $PtCl_3{\cdot}H_2O$ [59], 1/2$PtCl_4$ [59], $Ag(CN)_2$ [60]).

The nature of the hydrogen bonds apparently depends on the properties of the counterions, and appears to be weaker with hard and less basic counterions. With imidazolium ions and the corresponding amines and alcohols, the stable adducts **12** (R^1 = Mes, R^2 = H [26]), **13** (R^1 = Mes, R^2 = H [61]), and **14** (R^1 = Mes, R^2 = H [61]) are formed.



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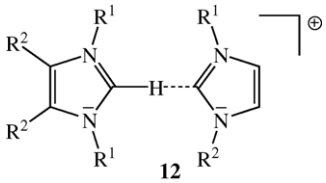

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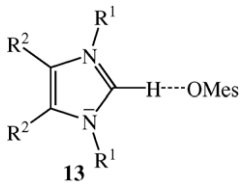

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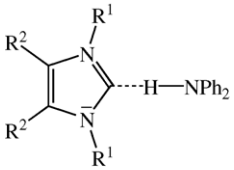

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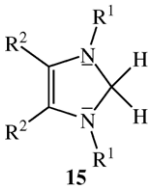
The carbenes **1** appear to be inert towards hydrogen under normal conditions [62] (for MO calculations see also [63]). The imidazolines **15** (R^1 = ^{t}Bu, Mes, R^2 = H) are conveniently obtained from the imidazolium salts **2** and $LiAlH_4$ [62], or by the thermal decomposition of an InH_3 adduct [64]. The corresponding compound **16** (R^1 = Neo [65]) has been synthesised by the reduction of the corresponding thione in THF using potassium (for MO calculations of the parent compound see [62]). The reaction of **1** with hydrogen (muonium) atoms to give the radicals **17** and **18** has been discussed by use of MO calculations as well as by muon spin rotation and muon level-crossing spectroscopy [66]. The intermolecular hydrogen transfer from **1** (R^1, R^2 = H) to imidazole has been investigated by computational methods [67].



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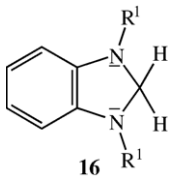

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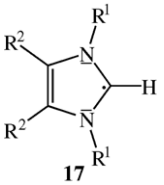

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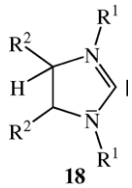

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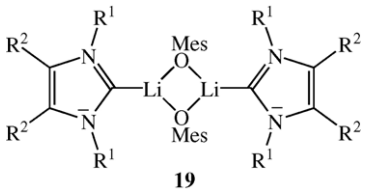
3. Reactions with group 1 element compounds

There are only rare examples of carbene **1** adducts at alkali metal centres. The adduct **19** (R^1 = ^{t}Bu, R^2 = H [68]) is formed by the reaction of **1** with LiOMes. Similarly, the adducts **20** (R^1 = ^{t}Bu, Ad, Mes, R^2 = H, R^3 = $SiMe_3$ [69]) are obtained from the carbenes **1** and $LiC_5H_2R^3{}_3$. The dinuclear chelate complex **22** (R = ^{t}Bu [70]) is formed by the reaction of the imidazolium salt **21** with ^{n}BuLi. The adducts **23**, **24**, and **25** (R^1 = ^{i}Pr, R^2 = H, R^3 = $SiMe_3$ [71]) have been obtained from the reaction of **1** with $MNR_2{}^3$ (M = Li, Na, K) in toluene, and have only been characterised by ^{13}C NMR in solution. The chemistry of the imidazolide–borane anion adducts of the type **26** [72–74] is not part of this review.



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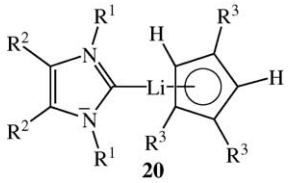

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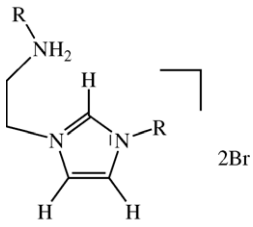

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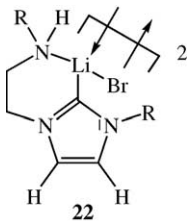

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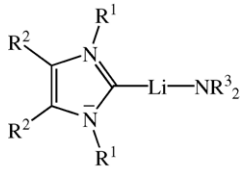

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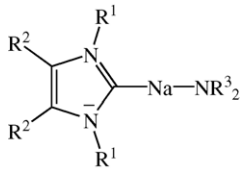

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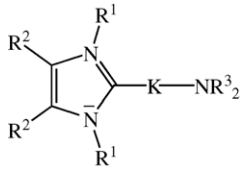

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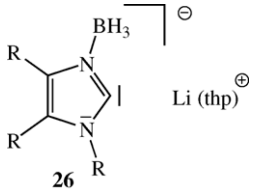

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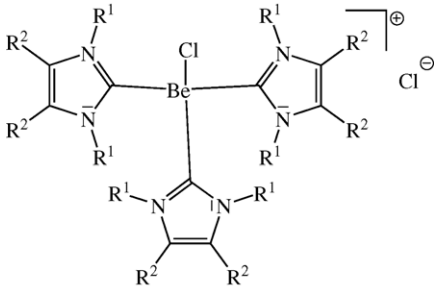
4. Reactions with group 2 element compounds

The tris(carbene) compound **27** (R^1 = Me, R^2 = H [75]) obtained from $BeCl_2$ and **1** is a unique example of a beryllium–imidazoline complex. Complexes **28** are formed from the reaction of Et_2Mg with the carbenes **1** (R^1 = Ad, Mes, R^2 = H [76]). Carbenes **1** react with group 2 metallocenes Cp_2M (M = Mg, Ca, Sr, Ba) and their solvate adducts to give the adducts **29** (R^1, R^2, R^3, R^4 = Me [77]; $R^1 = {}^i$Pr, R^2 = Me, R^3 = H, R^4 = Me; $R^1 = {}^i$Pr, R^2 = Me, $R^3 = SiMe_3$, $R^4 = {}^t$Bu [78]), **30** (R^1, R^2, R^3, R^4 = Me [77]; $R^1 = {}^i$Pr, R^2 = Me, R^3 = H, R^4 = Me; $R^1 = {}^i$Pr, R^2 = Me, $R^3 = {}^i$Pr, R^4 = Me [78]), **31** (R^1, R^2, R^3, R^4 = Me [77]; $R^1 = {}^i$Pr, R^2, R^3, R^4 = Me [78]) and **32** (R^1, R^2, R^3, R^4 = Me [77]; $R^1 = {}^i$Pr, R^2 = Me, $R^3 = {}^t$Bu, R^4 = Me [78]). The dicarbene complexes **33** and **34** (R^1, R^2, R^3, R^4 = Me [77]) prepared by the same method apparently require carbenes containing less bulky substituents.



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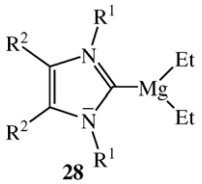

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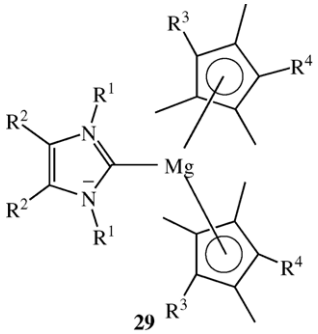

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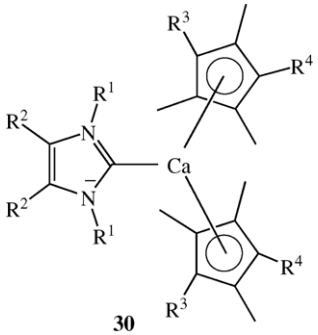

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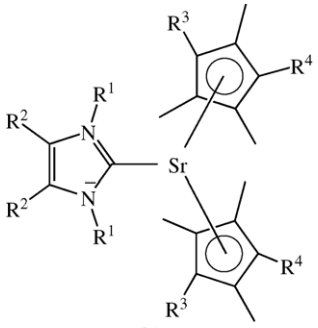

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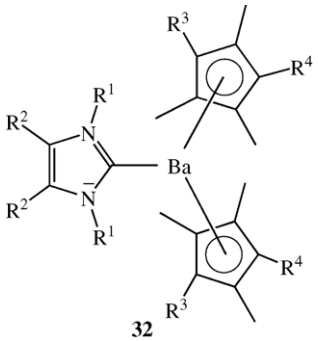

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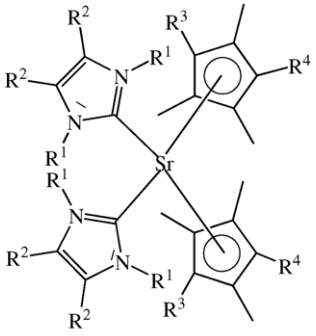

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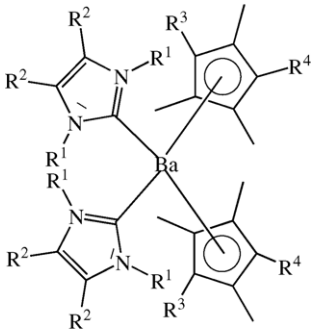

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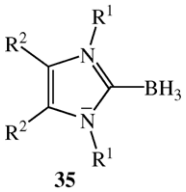
5. Reactions with group 13 element compounds

The carbenes **1** react with the adducts S·BX_3 (S = C_4H_8O, Et_2O, SMe_2; X = H, F) to give the complexes **35** (R^1 = Me, Et, ^{i}Pr, R^2 = Me [79]; R^1 = Mes, R^2 = H [80]) and **36** (R^1, R^2 = Me [79,81]; R^1 = Mes, R^2 = H, Cl [82]). An alternative route involves the reaction of the lithium salt of **37** with methyl iodide to give the complex **38** (R^1, R^2 = Me [72]). A further derivative of **38** (R^1 = Pr, R^2 = Me, R^3 = *p*-$CF_3CH_2CH_2SiMe_2C_6H_4$ [50]) is obtained by the hydrolysis of the corresponding imidazolium tetraarylborate salt. The dinuclear adduct **39** has also been reported [33]. When reacted with the boron heterocycles **40** and **41**, **1** gives the bicyclic compounds **42** (R^1 = Me, ^{i}Pr, R^2 = Me, R^3 = ^{t}Bu [83]) and **43** (R^1, R^2, R^3 = Me [84]). Borane adducts of the type **44** (e.g. [85]) are not part of this review.



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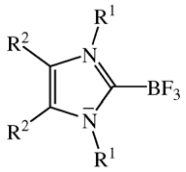

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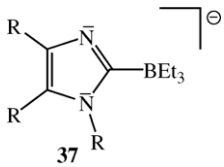

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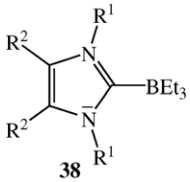

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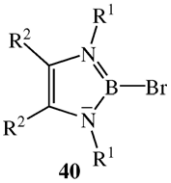

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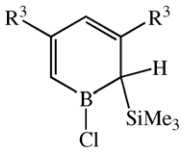

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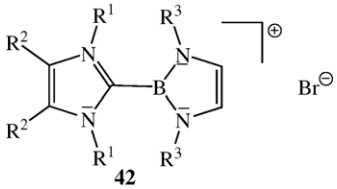

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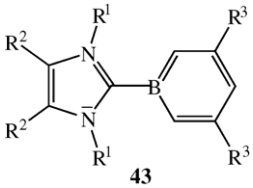

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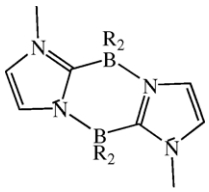
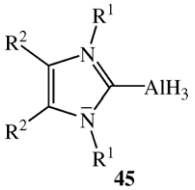


44

The alane adducts **45** (R^1 = Mes, R^2 = H [86]; R^1 = ^{i}Pr, R^2 = Me [87]; R^1 = 2,6-$^i Pr_2C_6H_3$, R^2 = H [54]) are obtained from the carbenes **1** and $LiAlH_4$ [54] or AlH_3·NMe_3 [86,87]. Similarly, the bifunctional carbene **46** reacts with AlH_3·NMe_3 to give the dinuclear complex **47** (R = ^{t}Bu [25]).

The trimethylalane complex **48** ($R^1 = {}^iPr$, $R^2 = Me$ [88]) is synthesized through the reaction of the carbene **1** with $AlMe_3$.



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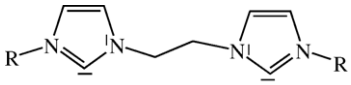

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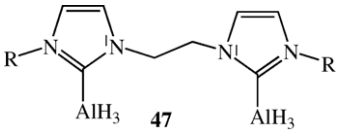

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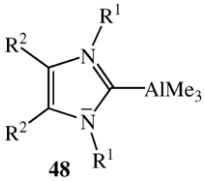
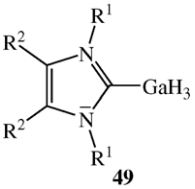


48

Reaction of the carbenes **1** with $LiGaH_4$ gives the gallane adducts **49** ($R^1 = Mes$, $R^2 = H$ [64]; $R^1 = {}^iPr$, $R^2 = Me$ [87]), while the dinuclear complex **50** ($R = {}^tBu$ [25]) is obtained from the carbene **46** and $GaH_3{\cdot}NMe_3$. The trimethylgallane complex **51** ($R^1 = {}^iPr$, $R^2 = Me$ [88]) is obtained from the reaction of the carbene **1** with $GaMe_3$. Reaction of the carbene **1** with "GaI" gives the anionic carbene complex **52** ($R^1 = Isi$, $R^2 = H$ [53]). The cyclopentadienylgallane adduct **53** is obtained from the reaction of the carbene **1** with $Cp^*{}_3Ga$ [89].



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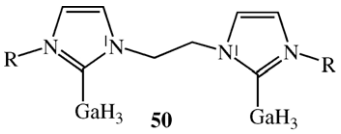

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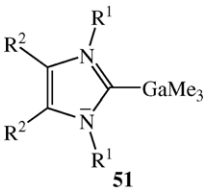

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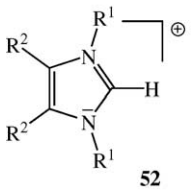

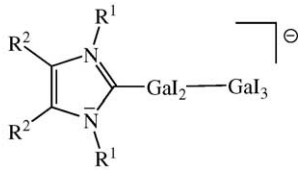

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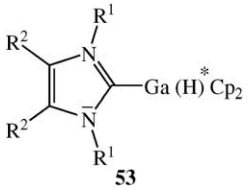
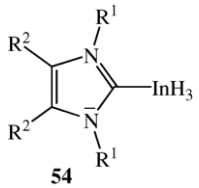


53

There has been a considerable interest in carbene indium complexes (for a comprehensive microreview see [90]). InH_3 adducts **54** ($R^1 = Mes$, $R^2 = H$, the InD_3 complex has also been mentioned [64]; $R^1 = {}^iPr$, $R^2 = Me$ [87,91]) are obtained from the carbenes **1** and $LiInH_4$ or $InH_3{\cdot}NMe_3$ [64,91]. Similarly, the dinuclear complex **55** ($R = {}^tBu$ [25]) is obtained from **46** and $LiInH_4$. Compound **54** ($R^1 = Mes$, $R^2 = H$) decomposes in toluene at 100 °C to give the carbene **1**, while the imidazoline **15** ($R^1 = Mes$, $R^2 = H$) is obtained in the presence of indium in tetrahydrofuran at 25 °C [64]. The reduction of ketones to alcohols by **54** ($R^1 = Mes$, $R^2 = H$) has also been reported [92]. The complex **58** ($R^1 = Mes$, $R^2 = H$ [64]) is obtained from **54** and quinuclidine·HCl or from the carbene **1** and $InH_2Cl{\cdot}(NMe_3)_n$.



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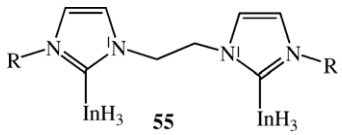

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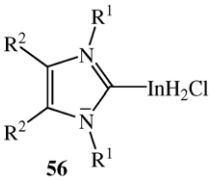

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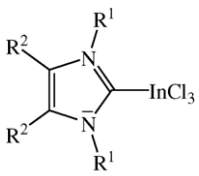

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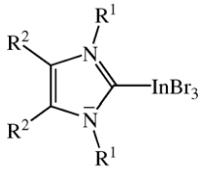
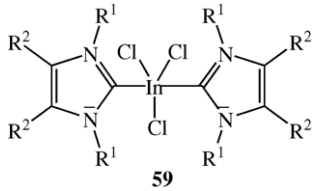


58

$InCl_3$ complexes **57** are obtained from the reaction of **54** with CH_2Cl_2 (R^1 = Mes, R^2 = H [64]) or from the carbene **1** and $InCl_3$ (R^1 = ^{i}Pr, R^2 = Me [55]). The reactions of $InBr_3$ with the carbenes **1** yield the complexes **58** (R^1 = Mes, Isi, R^2 = H [54]; R^1 = ^{i}Pr, R^2 = Me [55]). Similarly, the corresponding dicarbene complexes **59** and **60** (R^1 = ^{i}Pr, R^2 = Me [55]) are obtained in a similar fashion. In the presence of water, the anionic carbene complexes **61** and **62** are formed from **1** and the corresponding indium trihalides [55]. The chelate complex **63** (R = ^{t}Bu [25]) is prepared by the reaction of the bifunctional carbene **46** with $InBr_3$. InCl reacts with **1** in the presence of oxygen to form the cationic dinuclear complex **64** (R^1, R^2 = Me [53]), while with InBr, disproportionation occurs to give the dinuclear In(II) complex **65** (R^1 = Mes, R^2 = H [93]).



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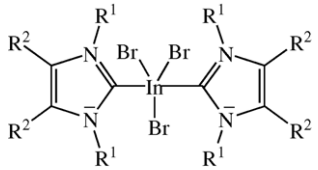

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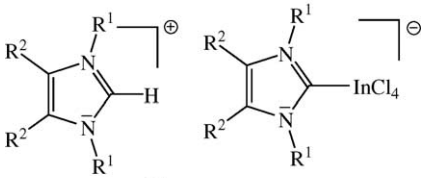

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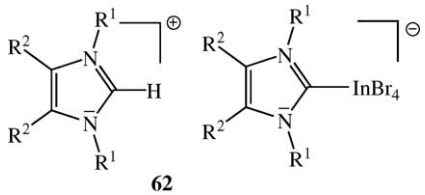

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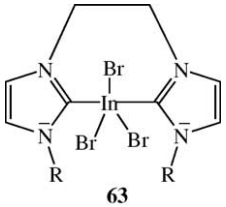

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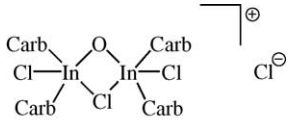

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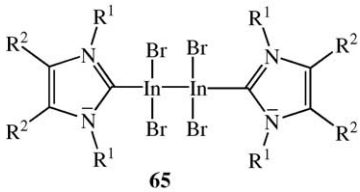
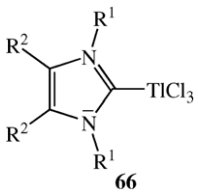


65

The carbene **1** reacts with TlX_3 to give the complexes **66** (R^1 = Mes, R^2 = H, Br [94]) and **67** (R^1 = Mes, R^2 = H [94]). With a further equivalent of **1**, the dicarbene complex **68** (R^1 = Mes, R^2 = H; R^1, R^2 = Me [94]) is formed by refluxing in mesitylene, and yields TlX and the corresponding 2-haloimidazolium halides as products [94]. The dinuclear complex **69** (R = ^{t}Bu [25]) is obtained from the bifunctional carbene **46** and $TlCl_3$. Similarly, **70** is obtained from the reaction of the corresponding carbene with CF_3SO_3Tl [95].



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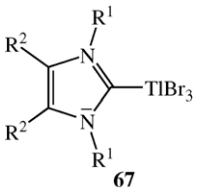

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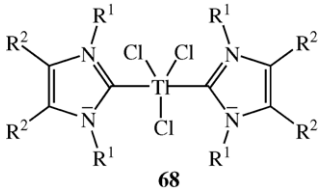

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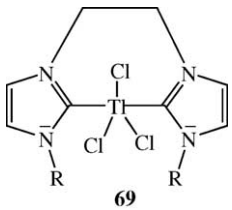

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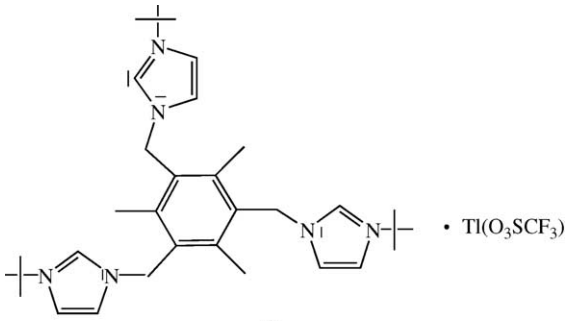

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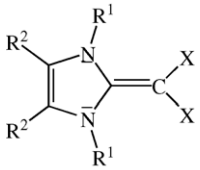

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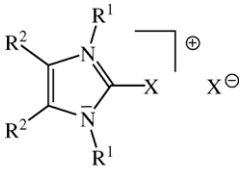
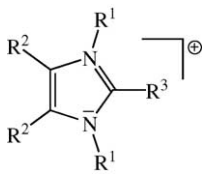


73

6. Reactions with group 14 element compounds

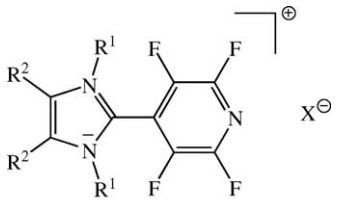
Numerous imidazolium compounds are known in which substituents are linked to the 2-position through C–C bonds [11]. In this section, only compounds directly obtained from 2,3-dihydroimidazol-2-ylidene (**1** and **7**) reactions are mentioned.

The alkylation of carbenes **1** is apparently a process complicated by side reactions. With MeI, **1** reacts to form a mixture of the corresponding 2H-imidazolium iodide and the iodide salt **71** ($R^1 = {}^i$Pr, R^2 = Me, R^3 = Me [31]), while EtI gives **71** ($R^1 = {}^i$Pr, R^2 = Me, R^3 = Et and CH(Me)Et [31]). On the other hand, the exclusive formation of the 2-methylimidazolium salt **71** (R^1 = 3,5-$Me_2C_6H_3$, R^2 = C≡CSiMe_3, R^3 = Me [96]) from the reaction of **1** and MeI has been reported. The chloride salts of **71** (R^1, R^2 = Me, $R^3 = CHX_2$ [97]) are obtained with $CHClX_2$ (X = F, Cl) by a complicated mechanism. This includes the formation of 2H-imidazolium salts and the methylene compounds **72** (R^1, R^2 = Me, X = F, Cl), which can be described as intermediates. With CCl_4, hydrogen/chlorine exchange of the 4,5-positions in **1** (R^1 = Mes, R^2 = H) occurs in the first step, while an excess of CCl_4 gives a mixture of **73** (R^1 = Mes, R^2, X = Cl, chloride salt) and **71** (R^1 = Mes, R^2 = Cl, X = Cl) [98]. From the reaction of **1** and 1,2-dichloroethane or hexachloroethane, the 2-chloroimidazolium chlorides **73** (R^1 = Me, Et, ^{i}Pr, R^2 = Me, X = Cl [24,99]) have been isolated as the only products (see also Chapter 9). The carbene **1** (R^1 = Mes, R^2 = H) also reacts with CBr_4 to give the corresponding 4,5-dibromocarbene **1** (R^1 = Mes, R^2 = Br), while a mixture of the imidazolium and 2-bromoimidazolium bromides is obtained with 1,2-$Br_2C_2H_4$ [30]. The reaction of **1** with CH_2 [100] and with CH_4 [101] has been investigated by computational methods.



71

Nucleophilic aromatic substitution of fluorine substituents has also been reported elsewhere. With pentafluoropyridine, **1** reacts to give the HF_2 salts **74** (R^1 = Me, ^{i}Pr, R^2 = Me) from which the imidazole **75** is obtained through thermolysis [102]. With 2-fluoro-1,3-diisopropyl-4,5-dimethylimidazolium tetrafluoroborate, **1** gives the dicationic salt **76** $R^1 = {}^i$Pr, R^2 = Me [103]) after addition of $BF_3 \cdot Et_2O$. Acylation of **1** occurs with PhC(O)F to give the fluoride salt **77** ($R^1 = {}^i$Pr, R^2 = Me), which gives the corresponding complex salts on addition of BF_3, $PhSiF_3$ and $PhSnF_3$ [104]. Surprisingly, the dicationic ketone **78** ($R^1 = {}^i$Pr, R^2 = Me [104]) is formed on reacting **1** with oxalylic chloride. The 2-cyanoimidazolium salts **79** ($R^1 = {}^i$Pr, R^2 = Me, X = Cl, $Ag(CN)_2$ [105]) are obtained from the corresponding 2-chloroimidazolium salt and KCN or AgCN.



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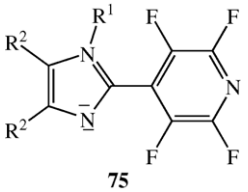

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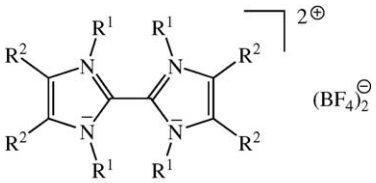

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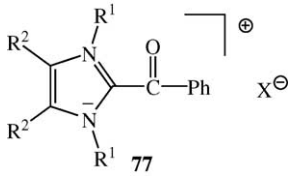

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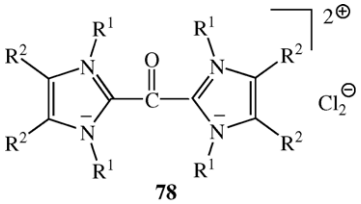

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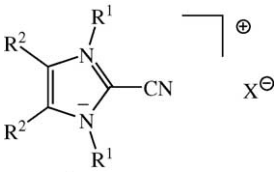
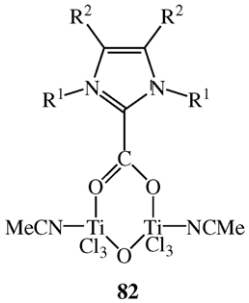


79

The carbene **1** readily reacts with carbon dioxide to give the zwitterionic adducts **80** (R^1 = Mes, Isi, R^2 = H [106]; R^1 = ^{i}Pr, R^2 = Me [107]). Reversible carboxylation of the carbenes **1** has been detected by use of thermogravimetric analysis and crossover experiments.[106] **80** reacts with HX, $[Et_3O]BF_4$, and $SOCl_2/AlCl_3$ to give the carboxylate derivatives **81** (R^1 = ^{i}Pr, R^2 = Me; X, Y = OH, Cl or BF_4; OEt, BF_4; Cl, $AlCl_4$ [107]). The carboxylic chloride reacts with methanol to give the ester **81** ((R^1 = ^{i}Pr, R^2 = Me; X, Y = OMe, Cl [107]). Coordination of **80** to $TiCl_4$ gives the dinuclear complexes **82** and **83** (R^1 = ^{i}Pr, R^2 = Me [108]). The crystal structure of **80** (R^1 = Me, R^2 = H [109]), obtained from the reaction of 1-methylimidazole with dimethyl carbonate, has been reported. The carboxylate **80** (R^1 = ^{t}Bu, R^2 = H [110]) is also formed by the reaction of **1** with $^1O_2$. The parent compound **80** (R^1, R^2 = H [111]) has been detected by irradiation of imidazole-2-carboxylic acid in matrix experiments.



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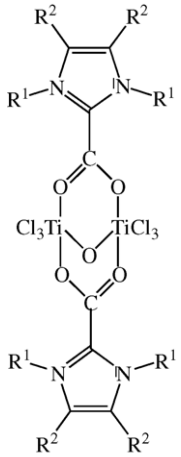
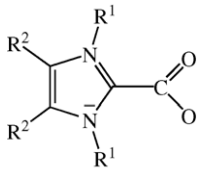
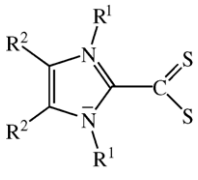


83

Similarly, the carbon disulfide adducts **84** (R^1 = Me, Et, ^{i}Pr, R^2 = Me [112], R^1 = $MeO(CH_2)_2$, $MeO(CH_2)_3$, R^2 = Me [113]; R^1 = 3,5-$Me_2C_6H_3$, R^2 = C≡CSiMe_3 [96]) have been obtained from isolated or in situ prepared carbenes **1** and CS_2. Reduction of **84** with potassium in tetrahydrofuran gives the salts **85** (R^1 = Me, Et, ^{i}Pr, R^2 = Me [114–116]), which react with MeI to give the 2-methyleneimidazolines **86** (R^1 = Et, ^{i}Pr, R^2 = Me [115]). Compound **84** reacts with bromine to give the salt **87** (R^1 = ^{i}Pr, R^2 = Me [112]), while with iodine, the charge transfer adduct **88** (R^1 = ^{i}Pr, R^2 = Me [112]) and the dicationic salt **89** (R^1 = ^{i}Pr, R^2 = Me [112]) are formed. The crystal structure of **84** (R^1 = Me, R^2 = H [117]) has been reported previously.



80



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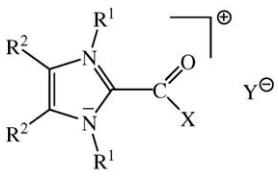

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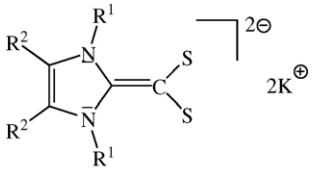

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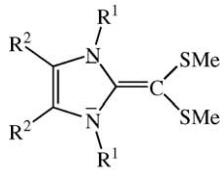
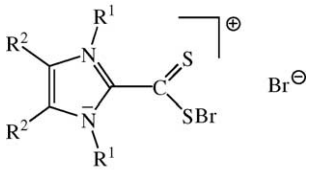


86



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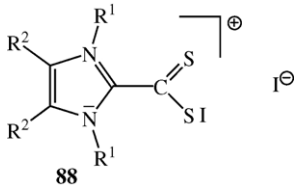
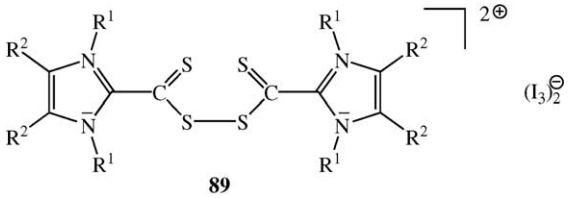
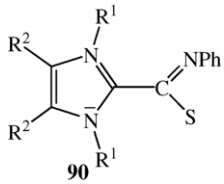


88

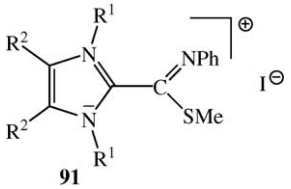


89

The formation of **90** (R^1 = Ph, R^2 = H [118]) from (in situ prepared) **1** and phenyl thiocyanate was reported more than 30 years ago. Its alkylation with methyl iodide to give the salt **91** has been reported [119]. Similarly, the in situ prepared carbene **7** gives the thiocyanate adduct **92** (R^1 = Bz [120]). With diisopropylcarbodiimide, **1** reacts to give the amidinate **93** (R^1, R^3 = ^{i}Pr, R^2 = Me [121]). Apparently, the reaction of **1** with carbon monoxide [122] was subsequently found to be false [123].



90



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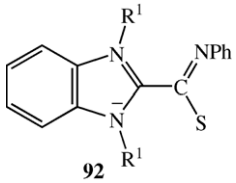
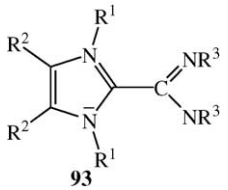
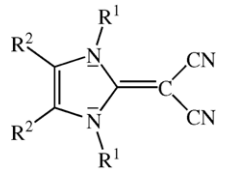


92

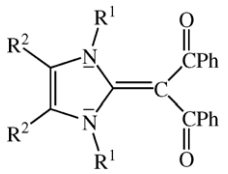


93

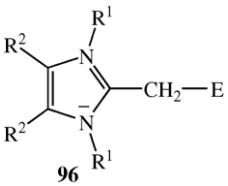
There are only rare examples of 2-methyleneimidazolines (**6**) formed directly from the carbenes **1**. 2-Haloimidazolium halides (see also Section 9) react with malodinitrile to give the olefins **94** (R^1 = Et, ^{i}Pr; R^2 = Me [124]), while **95** (R^1, R^2 = Me [124]) is obtained from **6** and benzoyl fluoride. The tetramethyl derivative (**6**, R^1, R^2 = Me [125]) is obtained through deprotonation of the corresponding pentamethylimidazolium salt [126], while the reaction of **1** with diazomethane gives the azine as the product of initial attack of the carbene at the terminal nitrogen atom (see Chapter 7). The chemistry of 2-methyleneimidazolines (**6**), which react with electrophiles E to give compounds of type **96**, has been reviewed elsewhere [7] (for more recent results see [127–130]). The dipyridoimidazolylidene **97** is reported to bond to the carbon atoms of carbon nanotubes [131].



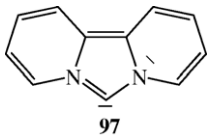
94



95



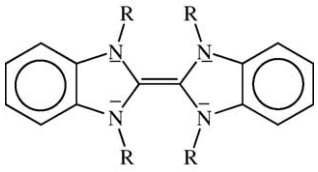
96



97

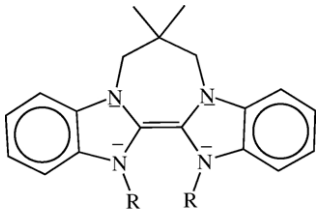
There has been considerable interest in the dimerisation of imidazol-2-ylidenes, which have been investigated by computational methods [67,132] (for a comrehensive discussion of the *Wanzlick* equilibrium see [133]), and the doubly bridged olefins, mentioned below, may also be formed by the dimerisation of the corresponding dinuclear carbenes. The equilibrium of **1** with its dimer has been studied by NMR and computational methods [134,135]. The dimerisa-

tion of the benzimidazol-2-ylidene **7** (R = Me, Ph), prepared in situ through deprotonation of the corresponding benzimidazolium salts, has been known for more than 30 years [136]. More recent reports of the preparation of **98** (R = Me, Neo [65]) start from the corresponding thione or use alternative cyclization reactions [137].



98

The bridged olefin **99** obtained from the thione reduction has also been reported [135]. The chemistry of the doubly bridged olefins has been reviewed elsewhere [138]. Compound **100** has been obtained from the electrochemical reduction of the dicationic salt **101** [139,140]. The olefins **102** ($n = 3$, 4) are prepared either by reduction, or deprotonation of the dicationic diimidazolium salts **103** or **104** [139,141–143]. Similarly, the olefin **105** is obtained from the salt **106** and sodium hydride [139]. Compounds **102** and **105** oxidize in air to give the corresponding ureaphanes (see Section 8) [139,141–143]. For **98** (R = Me [137]), **99** [135] and **102** ($n = 3$ [139,141–143]), the formation of transition metal carbene complexes is reported.



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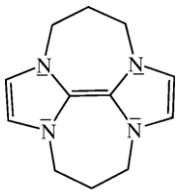

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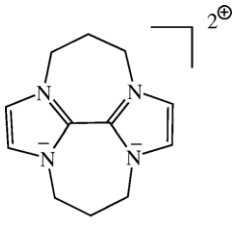
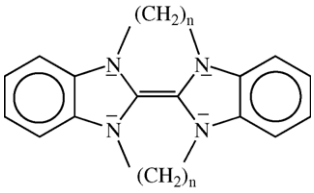
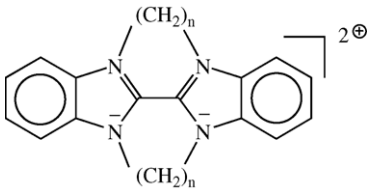


101



102



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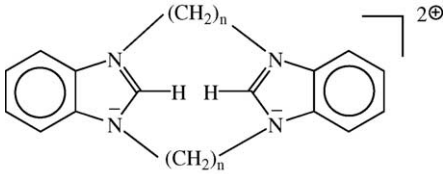

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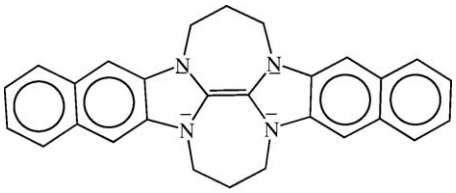

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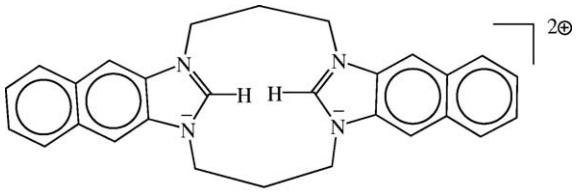
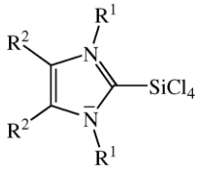
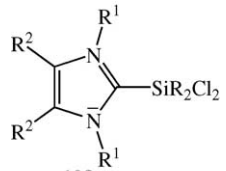


106

The carbene **1** reacts with $SiCl_4$ and R_2SiCl_2 to give the adducts **107** (R^1 = Me, Et, ^{i}Pr; R^2 = Me [144]) and **108** (R^1 = Et, ^{i}Pr; R^2 = Me; R^3 = Me, Ph [144]). With Me_3SiI, the salt **109** (R^1 = Et, R^2 = Me [144]) is obtained. Complex **112** (R^1, R^2 = Neo [145,146]) is obtained from the reaction of the carbene **7** (R^1 = Neo) with the silylene **111** (R = Neo, E = Si). Structure and bonding in the silylene adduct **113** (R^1, R^2 = H [100]) was investigated by computational methods.



107



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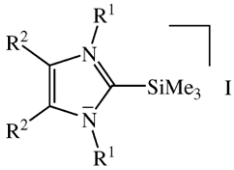

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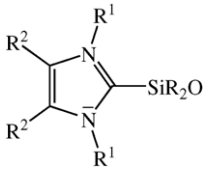

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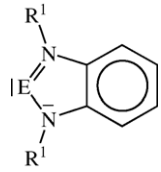

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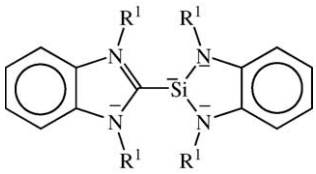

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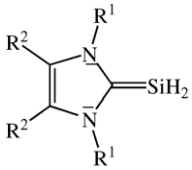
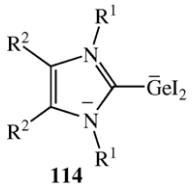
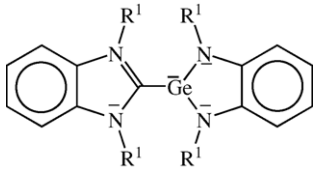


113

The adduct **114** (R^1 = Mes, R^2 = H [147]) is formed from **1** and GeI_2. When reacted with the germylene **111** (R = Neo, E = Ge), the carbene **7** (R^1 = Neo) gives the complex **115** (R^1, R^2 = Neo [146]). Structure and bonding in the germylene adduct **118** (R^1, R^2 = H [100]) was investigated by computational methods.



114



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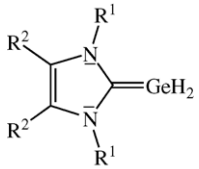

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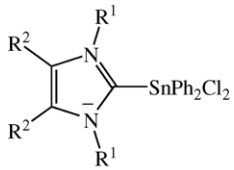

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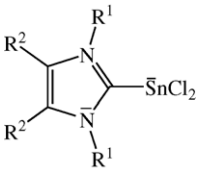
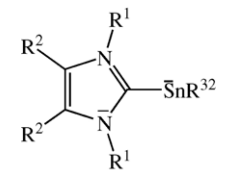


118

The adducts **117** (R^1 = Me, Et, ^{i}Pr; R^2 = Me [144]) are obtained from the reaction of **1** with Ph_2SnCl_2. The reaction of **1** with SnX_2 gives the complexes **118** (R^1 = ^{i}Pr, R^2 = Me [144]) and **119** (R^1 = ^{i}Pr, R^2 = Me, R^3 = 2,4,6-^{i}Pr$_3$C$_6$H$_2$ [148]). Compound **120** (R^1, R^2 = Neo [109]) is obtained from the reaction of the stannylene **111** (R = Neo, E = Sn) with carbene **7** (R^1 = Neo). Similarly, **120** (R^1 = Me, R^2 = $CH_2CH_2NMe_2$ [149]) is formed through the reaction of **98** (R = Me) with the stannylene **111** (E = Sn, R = $CH_2CH_2NMe_2$). Structure and bonding in the stannylene adduct **121** (R^1, R^2 = H [100]) was investigated by computational methods.



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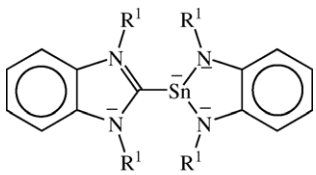

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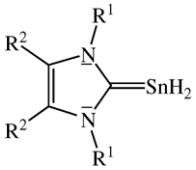
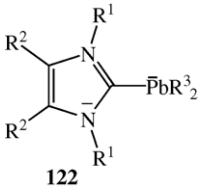
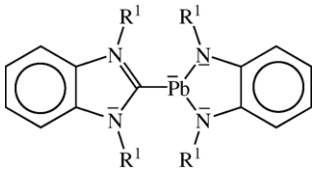


121

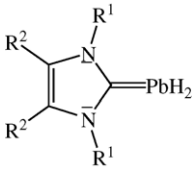
The carbene **1** reacts with $R_2Pb=PbR_2$ to give the plumbylene complex **122** ($R^1 = {}^{i}Pr$, $R^2 = Me$, $R^3 = 2,4,6\text{-}{}^{i}Pr_3C_6H_2$ [150]). The adduct **123** (R^1, $R^2 = Neo$) has been obtained from the reaction of the carbene **7** ($R^1 = Neo$) with the plumbylene **111** (R = Neo, E = Pb [146]). Structure and bonding in the plumbylene adduct **124** (R^1, $R^2 = H$ [100]) was investigated by computational methods.



122



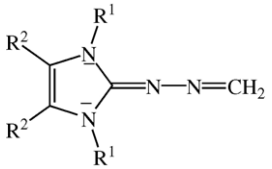
123



124

7. Reactions with group 15 element compounds

There are only rare examples of 2,3-dihydroimidazol-2-ylidene reactions from which carbon-nitrogen bonds are formed. The carbene **1** reacts with diazo compounds to give the azines **125** ($R^1 = Et$, $R^2 = Me$ [151], **126** ($R^1 = Mes$, $R^2 = H$ [152]) and **127** ($R^1 = Mes$, $R^2 = H$ [152]). Similarly, **128** ($R^1 = Me + Fc$ [47]) is obtained from the in situ prepared carbene **7**. With HN_3, the corresponding imidazolium azides are formed [151]. Trimethylsilyl azide reacts with **1** to give the imine **129** ($R^1 = Mes$, $R^2 = H$ [152]) in low yield, the source of hydrogen being unknown. A simple route to **129** ($R^1 = Me$, $R^2 = H$ [153]) not involving **1**, consists of the methylation of 2-amino-1-methylimidazole followed by deprotonation. Its extended chemistry, including the synthesis of the silyl derivative **130** ($R^1 = Me$, $R^2 = H$ [153]), and further compounds of the types **131** and **132**, has been reviewed recently [7,8] (for MO calculations see [7,8,100]).



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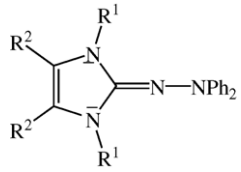

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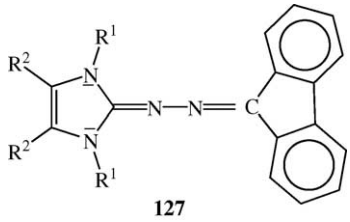

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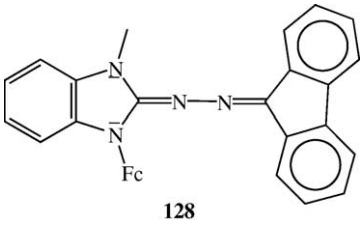

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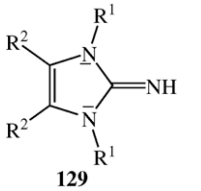

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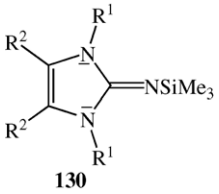

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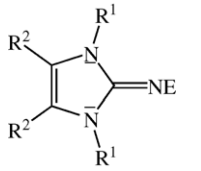

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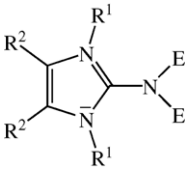
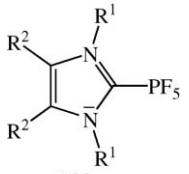


132

The carbene **1** reacts with PF_5 and $PhPF_4$ to give the phosphorane adducts **133** (R^1 = Mes, R^2 = H [154]) and **134** (R^1 = Mes, R^2 = H, Cl [82]). With $POCl_3$, the salt **135** ($R^1 = {}^i$Pr, R^2 = Me [155]) is formed which is transformed into the phosphenic chloride adduct **136** ($R^1 = {}^i$Pr, R^2 = Me [156]) and its acid **137** ($R^1 = {}^i$Pr, R^2 = Me [155]) by stepwise hydrolysis. With $PSCl_3$, regioselective desulfurisation occurs to give the corresponding thione **3** (R^1 = Me, Et, ^{i}Pr, R^2 = Me [15]) and PCl_3.



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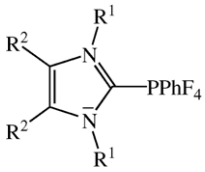

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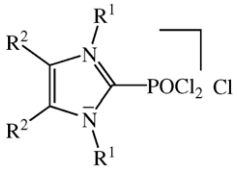

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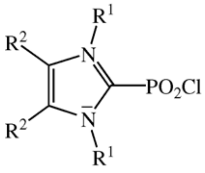

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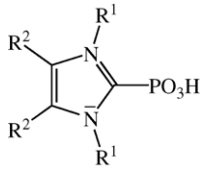
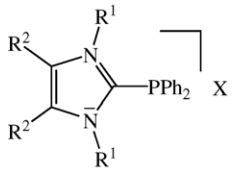


137

The cationic phosphanes **138** (R^1 = Me, R^2 = H, X = Cl, PF_6 [157]; $R^1 = {}^i$Pr, R^2 = Me, X = Cl, $AlCl_4$ [158]) are obtained from the reaction of isolated, or in situ prepared, **1** and Ph_2PCl. Different results have been obtained from hydrolysis, apparently depending on the nature of R^2 [157,158]. Compound **138** ($R^1 = {}^i$Pr, R^2 = Me) reacts with EtOH to give the corresponding imidazolium chloride and Ph_2POEt; and the phosphane selenide **139** ($R^1 = {}^i$Pr, R^2 = Me, X = $AlCl_4$) is formed with selenium [158]. Reaction of **138** ($R^1 = {}^i$Pr, R^2 = Me, X = Cl) with $(PhCN)_2MCl_2$ (M = Pd, Pt) gives the neutral complexes **140** and **141** ($R^1 = {}^i$Pr, R^2 = Me) [159]. The carbene adducts **142** ($R^1 = {}^i$Pr, R^2 = Me, X = Cl, CF_3SO_3 [160]) are obtained from **1** and the iminophosphines $Mes^*N{=}PX$.



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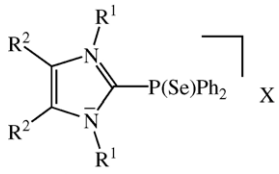

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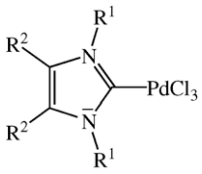

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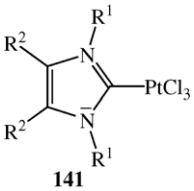

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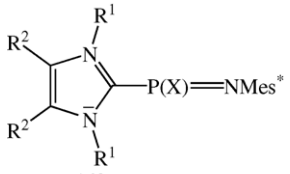
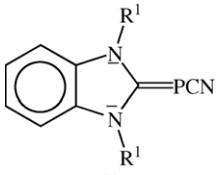


142

The cyanophosphinidene **143** (R^1 = Me [161]) was reported more than 20 years ago. The phosphinidenes **144** (R^1 = Mes, R^2 = H, R^3 = CF_3, Ph [162]; R^1, R^2 = Me, R^3 = Ph [163]) are obtained from the reaction of **1** and the phosphacycles $(R^3P)_n$ (n = 4,5). Compound **144** reacts with BH_3·THF to give the borane adduct **145** (R^1 = Mes, R^2 = H, R^3 = Ph [164]). MO calculations on **144** have been reported [100,165,166].



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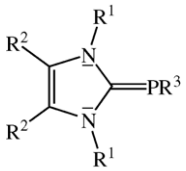

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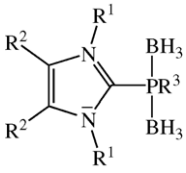
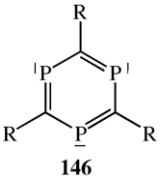


145

The carbene **1** reacts with **146** (R = ^{t}Bu) to give the olefin **147** (R^1, R^2 = Me), from which the tricarbonylmolybdenum complex **148** is formed with (Nor)Mo(CO)$_4$ [167]. Similarly, the carbene **7** (R^1 = Neo) reacts with ^{t}BuC≡P to give the olefin **149** (R^1 = Neo), while with ^{i}Pr$_2$NC≡P, the olefin **150** (R^1 = Neo) is formed.[168] **1** (R^1, R^2 = Me) reacts with ^{i}Pr$_2$NC≡P to give the phosphinidene **151**, from which the zwitterionic salts **152** and **153** are obtained on treatment with BH$_3$·THF and air [169].



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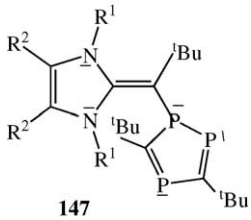

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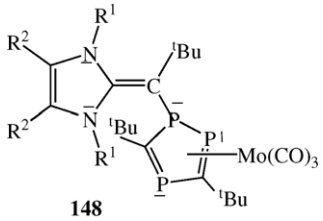

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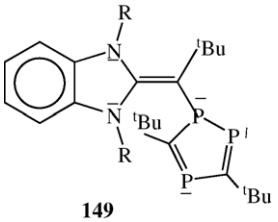

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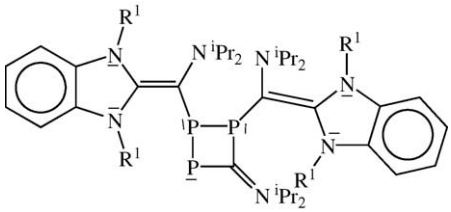

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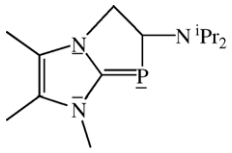

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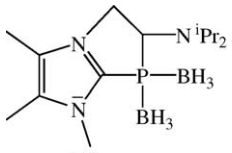

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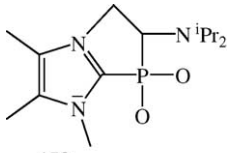
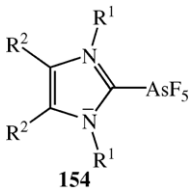


153

The arsorane derivative **154** (R^1 = Mes, R^2 = Cl [82]) is obtained from the reaction of **1** with AsF$_5$. **1** reacts with the arsacycles (R^3As)$_n$ (n = 4,6) to give the arsinidenes **155** (R^1 = Mes, R^2 = H, R^3 = Ph, C$_6$F$_5$ [162]). MO calculations on **155** (R^1, R^2, R^3 [100]) have been reported. The reaction of **1** with SbF$_5$ gives the stiborane adduct **156** (R^1 = Mes, R^2 = Cl [82]). The stibane derivative **157** (R^1 = Mes, R^2 = Cl [170]) is obtained from the reaction of **1** with Sb(CF$_3$)$_3$.



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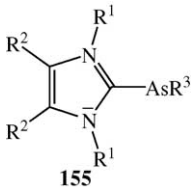

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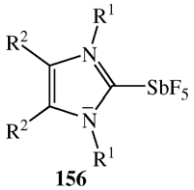

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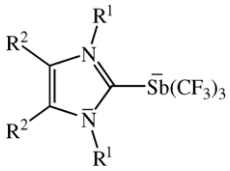

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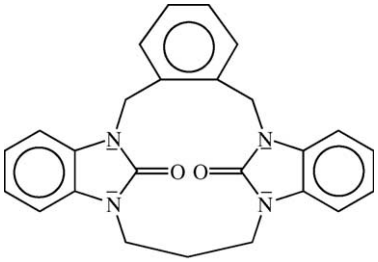
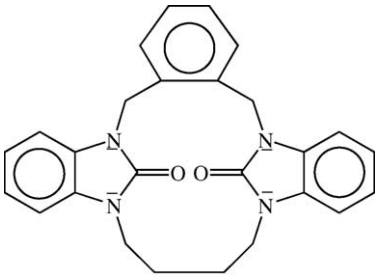


161

8. Reactions with group 16 element compounds

The carbenes **1** appear to be inert to $^3O_2$ attack under normal conditions, while NO causes the complete oxidation to the urea **158** [62]. In contrast, oxidation by air occurs to give the ureas **159**–**165** with the corresponding carbenes or their dimers [139,141–143]. Structure and bonding of **158** (R^1 = H, Me, R^2 = H) has been investigated by computational methods [7,100]. $^1O_2$ reacts with **1** to give the corresponding 1,2-diimine and the betaine **80** (R^1 = ^{t}Bu, R^2 = H) [110]. Slow hydrolysis of **1** (R^1 = ^{t}Bu, R^2 = H) has been reported to give the formamide **166** [62]; for further comments on the hydrolysis see [118] (The reaction of **1** with D_2O and 2,4,6-trimethylphenol has been mentioned in Chapter 2). Thiones **3** and selones **4** form numerous adducts with halogens and pseudohalogens (E = S, Se; **167** and **168**), which have been reviewed elsewhere [6] (for more recent work see [171], see also [172,173]) and are not reviewed in this report.



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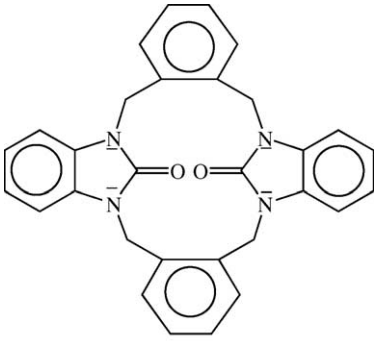

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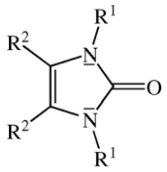

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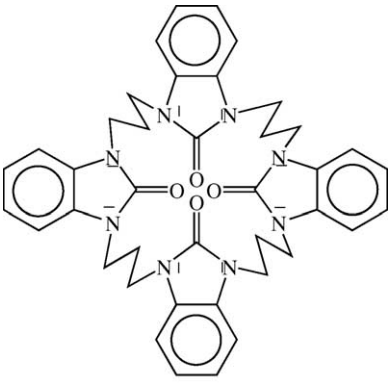

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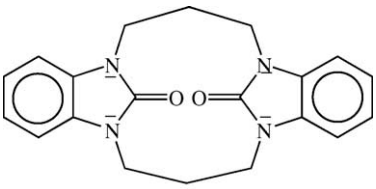

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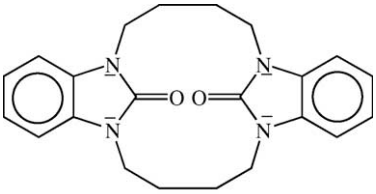

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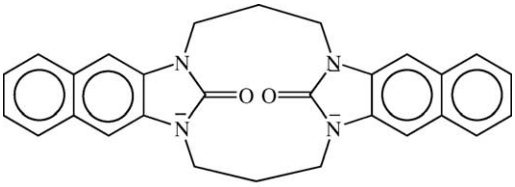

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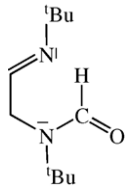
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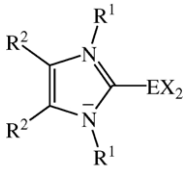
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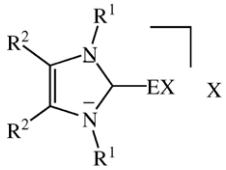
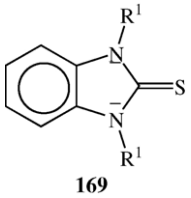

168

In addition to other synthetic routes (see e.g. [4]), thiones **3** (R^1 = Me, R^2 = H [174]; R^1 = Fc, R^2 = H [51]) and their benzimidazole derivatives **169** and **170** [47,120,175,176] are obtained from the direct reaction of isolated or in situ prepared carbenes with elemental sulfur or from **1** (R^1 = Mes, Ad, R^2 = H) and R_3ES (E = As, Sb). [177] Similarly, **3** is obtained from the reaction of **1** (R^1 = Me, Et, ^{i}Pr; R^2 = Me) with $PSCl_3$ in quanitative yields.[15] Dehydrogenation of the corresponding imidazolidin-2-thiones has also been reported.[178] Structure and bonding of **3** (R^1 = H, Me, R^2 = H [7,100]) has been investigated by computational methods. For calorimetric studies on the sulfur binding to **1** see [177].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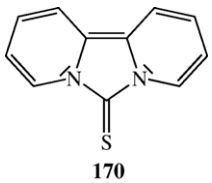
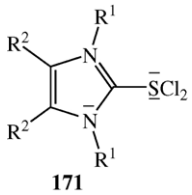

170

The carbene **1** reacts with SCl_2 and $SOCl_2$ to give the adduct **171** (R^1 = ^{i}Pr, R^2 = Me [179]) from which the SF_2 derivative **172** (R^1 = ^{i}Pr, R^2 = Me [179]) is obtained with AgF. When reacted with $SOCl_2$, **1** gives the adduct **173** (R^1 = ^{i}Pr, R^2 = Me [179]), from which the salt **174** (R^1 = ^{i}Pr, R^2 = Me [179]) is formed when reacted with MeI. For reactions of **1** with sulfuric halides see Chapter 9.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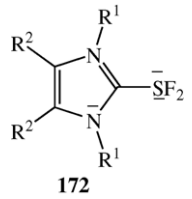
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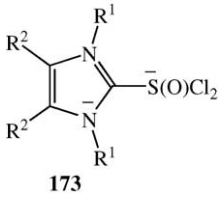
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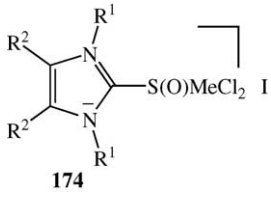
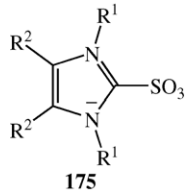

174

The formation of a stable adduct from the reaction of **1** with SO_2 [180] has subsequently been questioned [181]. The SO_3 adduct **175** (R^1 = ^{i}Pr, R^2 = Me [182]) is obtained from the reaction of the 2-chloroimidazolium chlorosulfite salt (see Chapter 9) with aqueous KCN. **175** reacts with HX to give the cationic acids **176** (R^1 = ^{i}Pr, R^2 = Me, X = BF_4, SbF_6 [155]).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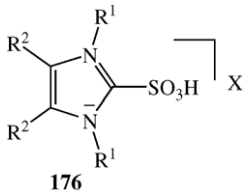
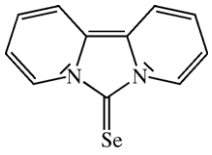

176

The selones **4** (R^1 = Me, R^2 = H [173]; R^1 = Me, Et, ^{i}Pr, R^2 = Me [183]) and **177** [176] are obtained from isolated, or in situ prepared, carbenes and selenium. Structure and bonding of **4** (R^1 = Me, R^2 = H [7]) has been investigated by computational methods. Similarly, the tellones **178** (R^1 = Mes, R^2 = H, Cl [98]; R^1 = Me, Et, ^{i}Pr, R^2 = Me [184]) and **179** [176] are obtained from the corresponding carbenes and tel-

lurium. **178** reacts with iodine to give **180** (R^1 = Et, R^2 = Me [185]), which is also obtained from the reaction of **1** (R^1 = ^{i}Pr, R^2 = Me) with TeI_4 [186].



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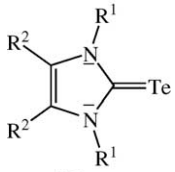

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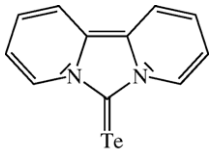
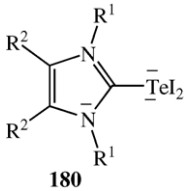


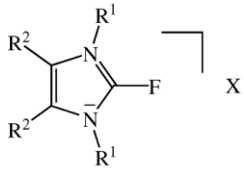
179



180

9. Reactions with group 17 element compounds

There are a couple of reports describing the reaction of **1** with halogens or halogen compounds yielding the salts **181** – **184**. Weak interionic interaction (**185**, X = Cl, Br, I) has been discussed for the salts of "soft" anions. 2-Fluoroimidazolium salts **181** (R^1 = ^{i}Pr, R^2 = Me, X = SF_3, SO_2F [179]) are obtained from **1** and SF_4 or SO_2F_2. Anion exchange with BF_3·Et_2O is reported to give the BF_4 salt (R^1 = ^{i}Pr, R^2 = Me, X = BF_4 [102]). For nucleophilc aromatic substitution in **1** see Section 6.



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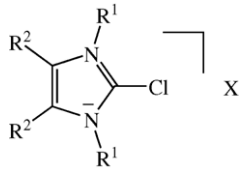
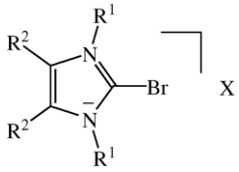


182



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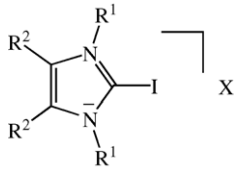

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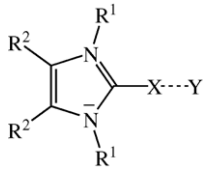
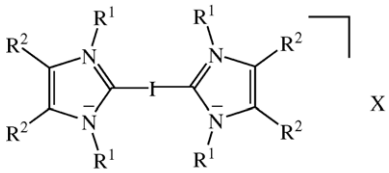


185

Chloride salts of **182** (R^1 = Mes, R^2 = H [30,94]; R^1 = Mes, R^2 = Cl [98]; R^1 = Me, Et, ^{i}Pr, R^2 = Me [24,99]) are formed from the reaction of **1** and CCl_4 [98], 1,2-$Cl_2C_2H_4$ [24] and C_2Cl_6 [30,99] or by thermal decomposition of **66** (R^2 = H) [94]. The structure of a hydrate salt has also been reported [24]. Additional salts of **182** (R^1 = ^{i}Pr, R^2 = Me, X = SO_2F, SO_2Cl [179,187], PO_2Cl_2 [188], $AlCl_4$ [24,30], 1/2$TeCl_6$ [189], $Ag(CN)_2$ [105]) are obtained from the reaction of **1** with SO_2Cl_2 [187] or SO_2ClF [179], and from the reaction of the chloride salts with SO_2 [24], $POCl_3$ (in the presence of water) [188], $AlCl_3$ [24,30], $TeCl_4$ [189], or AgCN [105].

The bromide salts of **183** (R^1 = Mes, R^2 = H, X = Br [30,94]; R^1 = ^{i}Pr, R^2 = Me, X = Br [190]) are obtained from the reaction of **1** with Br_2 [30,190] or 1,2-$Br_2C_2H_4$ [30] and by thermal decomposition of **67** (R^2 = H) [94]. The crystal structure of the solvate adduct **183** (R^1 = ^{i}Pr, R^2 = Me, X = Br·CBr_4 has also been reported [190]. The bromide salt reacts with $TeBr_4$ to give the corresponding $TeBr_5$ [190] and $TeBr_6$ [189] salts (see Chapter 6 for the formation of **94**).

The iodide salts of **184** (R^1 = Mes, R^2 = H [191]; R^1 = Et, R^2 = Me [192]) are formed by reacting **1** with iodine. Reaction of the salts **184** with the carbene **1** gives the iodonium compounds **186** (R^1 = Mes, R^2 = H, X = I, BPh_4 [191]). The triiodide salts **184** (R^1 = ^{i}Pr, R^2 = Me; X = I_3 [193]) and **187** [27] are obtained by reacting the corresponding carbenes **1** with iodine. With C_6F_5I, **1** forms the adduct **188** (R^1 = Ad, R^2 = H [194]), while adduct **189** (R^1 = ^{i}Pr, R^2 = Me [195]) is obtained with Br–C_2F_4–I.



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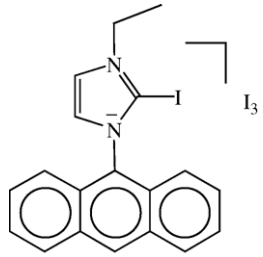
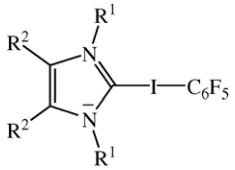


187



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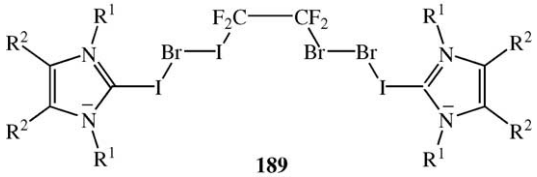

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Synthesis

A	Reaction of isolated or in situ prepared carbene with E or its derivatives
B	Exchange of 2-substituents in imidazolium cations with E or its derivatives
C	Chemical alterations in the E substituents of carbene adducts
D	Further methods

10. Table of Compounds

Derivatives of **1** (R^1, R^2) and **7** (R^1,–), **8** and **9**, and further 2,3-dihydroimidazol-2-ylidenes are listed in the following table if they are obtained from the corresponding carbenes or their reaction products. See end of table for abbreviations.

E	R^1	R^2	Syn	Instrumental analysis	Ref.
H–O–2,6-^{t}Bu$_2$-4–Me–C$_6$H$_2$	Mes	H	A	^{1}H, X-ray	[61]
H–NPh$_2$	Mes	H	A	^{1}H, X-ray	[61]
^{b}H–Carb$^+$PF$_6^-$	Mes	H	A	^{1}H, ^{13}C, X-ray	[26]
H$_2$	^{t}Bu	H	A	^{1}H, ^{13}C, IR	[62]
H$_2$	Mes	H	B	^{1}H, ^{13}C, MS, IR	[64]
H$_2$	Neo	–	(A), D	^{1}H, ^{13}C	[65]
22	–	–	A	^{1}H, ^{13}C, X-ray	[70]
Li-Omes^c	^{t}Bu	H	A	X-ray	[68]
Li–N(SiMe$_3$)$_2$	^{i}Pr	Me	A	^{13}C	[71]
Li–1,2,4–(Me$_3$Si)$_3$C$_5$H$_2$	^{t}Bu	H	A	^{1}H, ^{7}Li, ^{13}C, ^{29}Si, X-ray	[69]
Li–1,2,4-(Me$_3$Si)$_3$C$_5$H$_2$	Ad	H	A	^{1}H, ^{7}Li, ^{13}C, ^{29}Si	[69]
Li–1,2,4-(Me$_3$Si)$_3$C$_5$H$_2$	Mes	H	A	^{1}H, ^{7}Li, ^{13}C, ^{29}Si	[69]
Na–N(SiMe$_3$)$_2$	^{i}Pr	Me	A	^{13}C	[71]
K–N(SiMe$_3$)$_2$	^{i}Pr	Me	A	^{13}C	[71]
^{d}Be(Carb)$_2$Cl$^+$Cl$^-$	Me	H	A	^{1}H, ^{9}Be, ^{13}C, ^{14}N, IR, X-ray	[75]
MgEt$_2$	Ad	H	A	^{1}H, ^{13}C, ^{15}N,	[76]
MgEt$_2$	Mes	H	A	^{1}H, ^{13}C, ^{15}N, X-ray	[76]
Mg(C$_5$Me$_5$)$_2$	Me	Me	A	^{1}H, ^{13}C, X-ray	[77]
Mg(1-^{t}Bu-3–SiMe$_3$C$_5$H$_3$)$_2$	^{i}Pr	Me	A	^{1}H, ^{13}C, MS	[78]
Mg(Me$_4$C$_5$H)$_2$	^{i}Pr	Me	A	^{1}H, ^{13}C, MS, X-ray	[78]
Ca(C$_5$Me$_5$)$_2$	Me	Me	A	^{1}H, ^{13}C, X-ray	[77]
Ca(Me$_4$C$_5$H)$_2$	^{i}Pr	Me	A	^{1}H, ^{13}C, MS, X-ray	[78]
Ca(Me$_4$C$_5$^{i}Pr)$_2$	^{i}Pr	Me	A	^{1}H, ^{13}C, MS, X-ray	[78]

E	R^1	R^2	Syn	Instrumental analysis	Ref.
$Sr(C_5Me_5)_2$	Me	Me	A	^1H, ^{13}C	[77]
$Sr(C_5Me_5)_2$	^{i}Pr	Me	A	^1H, ^{13}C, MS, X-ray	[78]
$Sr(C_5Me_5)_2$(Carb)[e]	Me	Me	A	^1H, ^{13}C, X-ray	[77]
$Ba(C_5Me_5)_2$	Me	Me	A	^1H, ^{13}C, X-ray	[77]
$Ba(Me_4C_5{}^tBu)_2$	^{i}Pr	Me	A	^1H, ^{13}C, MS, X-ray	[78]
$Ba(C_5Me_5)_2$(Carb)[e]	Me	Me	A	^1H, ^{13}C	[77]
BH_3	Mes	H	A	X-ray, MO	[80]
BH_3	Me	Me	A	^1H, ^{11}B, ^{13}C	[79]
BH_3	Et	Me	A	^1H, ^{11}B, ^{13}C, X-ray, MO	[79]
BH_3	^{i}Pr	Me	A	^1H, ^{11}B, ^{13}C	[79]
BF_3	Mes	H	A	^1H, ^{11}B, ^{13}C, ^{19}F, X-ray	[82]
BF_3	Mes	Cl	A	^1H, ^{11}B, ^{13}C, ^{19}F, X-ray	[82]
BF_3	Me	Me	A	^1H, ^{11}B, ^{13}C, ^{19}F, X-ray	[79,81]
BF_3	(see **39**)		D	^1H, ^{13}C, ^{19}F, MS, X-ray	[33]
BEt_3	Me	Me	D	^1H, ^{11}B, ^{13}C, MS	[72]
$B(C_6H_4SiMe_2CH_2CH_2CF_3)_4$	Bu	Me	D	^1H, ^{11}B, ^{13}C, X-ray	[50]
$BC_{10}H_{20}N_2$ (see **42**)	Me	Me	A	^1H, ^{11}B, ^{13}C, IR, MS, X-ray	[83]
$BC_{10}H_{20}N_2$ (see **42**)	Me	Me	A	^1H, ^{11}B, ^{13}C, IR, MS	[83]
BC_7H_9 (see **43**)	Me	Me	A	^1H, ^{11}B, ^{13}C, MS, X-ray, MO	[84]
AlH_3	Mes	H	A	^1H, ^{13}C, ^{15}N, ^{27}Al, X-ray	[86]
AlH_3	Isi	H	A	^1H, ^{13}C, IR, MS, X-ray	[54]
AlH_3	^{i}Pr	Me	A	^1H, ^{13}C, ^{27}Al, IR, MS, X-ray	[87]
AlH_3	(see **47**)		A	^1H, ^{13}C, IR, MS, X-ray	[25]
$AlMe_3$	^{i}Pr	Me	A	^1H, ^{13}C, IR, X-ray	[88]
GaH_3	Mes	H	A	^1H, ^{13}C, IR, MS	[64]
GaH_3	^{i}Pr	Me	A	^1H, ^{13}C, IR, MS, X-ray	[87]
GaH_3	(see **50**)		A	^1H, IR, MS	[25]
GaI_2–$GaI_3{}^-$ ($CarbH^+$)[f]	Isi	H	A	^1H, ^{13}C, IR, MS, X-ray	[53]
$GaMe_3$	^{i}Pr	Me	A	^1H, ^{13}C, IR, X-ray	[88]
$Ga(H)Cp^*{}_2$	Me	Me	A	^1H, ^{13}C, MS, X-ray	[89]
InH_3	Mes	H	A	^1H, ^{13}C, IR, MS, X-ray	[64]
InH_3	^{i}Pr	Me	A	^1H, ^{13}C, IR, X-ray	[87,91]
InH_3	(see **55**)		A	^1H, IR, X-ray	[25]
InD_3	Mes	H	A	^1H, ^{13}C, IR, MS	[64]
InH_2Cl	Mes	H	A, C	^1H, ^{13}C, IR, MS, X-ray	[64]
$InCl_3$	Mes	H	C	^1H, ^{13}C, MS, IR, X-ray	[64]
$InCl_3$	^{i}Pr	Me	A	^1H, ^{13}C, IR, MS	[55]
$InCl_3$(Carb)[g]	^{i}Pr	Me	A	^1H, ^{13}C, IR, MS, X-ray	[55]
$InCl_4{}^-$ ($CarbH^+$)[g]	^{i}Pr	Me	A	^1H, ^{13}C, ^{115}In, MS, IR, X-ray	[55]
$InBr_3$	Mes	H	A	^1H, ^{13}C, IR, MS, X-ray	[54]
$InBr_3$	Isi	H	A	^1H, ^{13}C, MS, IR, X-ray	[54]
$InBr_3$	^{i}Pr	Me	A	^1H, ^{13}C, IR, MS, X-ray	[55]

E	R^1	R^2	Syn	Instrumental analysis	Ref.
$InBr_3$(Carb)[g]	^{i}Pr	Me	A	^{1}H, ^{13}C, IR, MS, X-ray	[55]
$InBr_4^-$ ($CarbH^+$)[g]	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{115}In, MS, IR, X-ray	[55]
63	–	–	A	^{1}H, ^{13}C, IR, MS, X-ray	[25]
$InBr_2$–$InBr_2$(Carb)[g]	Mes	H	A	^{1}H, IR, MS, X-ray	[93]
64	–	–	A	^{1}H, IR, MS, X-ray	[53]
70	–	–	A	^{1}H, ^{13}C, X-ray	[95]
$TlCl_3$	Mes	H	A	^{1}H, ^{13}C, IR, MS, X-ray	[94]
$TlCl_3$	Mes	Br	A	–	[94]
$TlCl_3$(Carb)[f]	Mes	H	A	^{1}H, ^{13}C, IR, MS	[94]
$TlCl_3$	(see **69**)		A	^{1}H, IR, MS	[25]
$TlBr_3$	Mes	H	A	–	[94]
Me^+I^-	Xyl	Syl	A	–	[96]
$CHF_2^+Cl^-$	Me	Me	A	^{1}H, ^{13}C, X-ray	[97]
$CHF_2^+BPh_4^-$	Me	Me	C	^{1}H, ^{13}C	[97]
$CHCl_2^+Cl^-$	Me	Me	A	^{1}H	[97]
$CHCl_2^+BPh_4^-$	Me	Me	C	^{1}H, ^{13}C, X-ray	[97]
Et^+I^-	^{i}Pr	Me	A, C	^{1}H, ^{13}C, X-ray	[31]
$CH(Me)Et^+I^-$	^{i}Pr	Me	C	^{1}H, ^{13}C	[31]
$C_5NF_4^+HF_2^-$ (see **74**)	Me	Me	A	^{1}H, ^{13}C, ^{19}F	[102]
$C_5NF_4^+HF_2^-$ (see **74**)	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{19}F	[102]
$C_5NF_4^+Cl^-$ (see **75**)	^{i}Pr	Me	C	X-ray	[102]
$C_{11}H_{20}N_2^{2+}(BF_4)_2^-$ (see **76**)	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{19}F, X-ray	[103]
CN^+Cl^-	^{i}Pr	Me	B	^{1}H, ^{13}C, MS, IR	[105]
$CN^+Ag(CN)_2^-$	^{i}Pr	Me	B	^{1}H, ^{13}C, MS, IR	[105]
$C(O)Ph^+F^-$	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{19}F, IR, MS	[104]
$C(O)Ph^+BF_4^-$	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{19}F, IR, MS	[104]
$C(O)Ph^+Ph_3\ SiF_2^-$	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{19}F, IR, MS	[104]
$C(O)Ph^+Ph_3\ SnF_2^-$	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{19}F, IR, MS, X-ray	[104]
$C(O)C_{11}H_{20}N_2^{2+}Cl_2^{2-}$(see **78**)	^{i}Pr	Me	A	^{1}H, ^{13}C, IR, MS, X-ray	[104]
CO_2	H	H	D	IR, MO	[111]
CO_2	Me	H	D	X-ray	[109]
CO_2	Mes	H	A	^{1}H, ^{13}C, IR	[106]
CO_2	Isi	H	A	^{1}H, ^{13}C, IR, X-ray	[106]
CO_2	^{t}Bu	H	D	–	[110]
CO_2	^{i}Pr	Me	A	^{1}H, ^{13}C, IR, MS, X-ray	[107]
$COOH^+Cl^-$	^{i}Pr	Me	C	^{1}H, ^{13}C, IR,	[107]
$COOH^+BF_4^{--}$	^{i}Pr	Me	C	^{1}H, ^{13}C, ^{19}F IR,	[107]
$COOMe^+Cl^-$	^{i}Pr	Me	C	^{1}H, ^{13}C, IR,	[107]
$COOEt^+BF_4^-$	^{i}Pr	Me	C	^{1}H, ^{13}C, IR,	[107]
$COCl^+SOCl_3^-$	^{i}Pr	Me	C	^{1}H, ^{13}C, IR,	[107]
$COCl^+AlCl_4^-$	^{i}Pr	Me	C	^{1}H, ^{13}C, ^{27}Al, IR,	[107]
$CO_2{\cdot}TiCl_4$	^{i}Pr	Me	C	IR	[108]

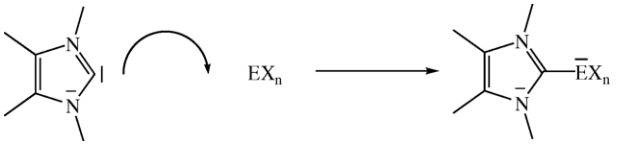
E	R^1	R^2	Syn	Instrumental analysis	Ref.
82	^{i}Pr	Me	C	^{1}H, IR, X-ray	[108]
83	^{i}Pr	Me	C	^{1}H, IR, X-ray	[108]
CS_2	Me	H	–	X-ray	[117]
CS_2	Me	Me	A	^{1}H, ^{13}C, IR, MS	[112]
CS_2	Et	Me	A	^{1}H, ^{13}C, IR, MS, X-ray	[112]
CS_2	^{i}Pr	Me	A	^{1}H, ^{13}C, IR, MS	[112]
CS_2	$(CH_2)_2OMe$	Me	A	^{1}H, ^{13}C, MS, X-ray	[113]
CS_2	$(CH_2)_3OMe$	Me	A	^{1}H, ^{13}C, MS, X-ray	[113]
CS_2	Xyl	Syl	A	–	[96]
$CS_2Br^+Br_3^-$	^{i}Pr	Me	C	^{1}H, ^{13}C, X-ray	[112]
$CS_2 \cdots I_2$	^{i}Pr	Me	C	^{1}H, ^{13}C, MS, X-ray	[112]
89	^{i}Pr	Me	C	^{1}H, ^{13}C, X-ray	[112]
C(S)NPh	Ph	H	A	^{1}H, IR	[118]
C(S)NPh	Bz	H	A	^{1}H, ^{13}C, IR, MS	[120]
$C(SMe)NPh^+I^-$	Ph	H	A	^{1}H, IR	[119]
$C(N^iPr)_2$	^{i}Pr	Me	A	^{1}H, ^{13}C, IR, MS, X-ray	[121]
CH_2	Me	Me	C	^{1}H, ^{13}C, MS, X-ray, MO	[7,125]
147	Me	Me	A	^{31}P, MO	[167]
148	Me	Me	C	X-ray, MO	[167]
149	Neo	–	(A)	^{1}H, ^{13}C, ^{31}P, MS, X-ray	[168]
150	Neo	–	(A)	^{1}H, ^{13}C, ^{31}P, MS, X-ray	[168]
98	Me	–	A, D	^{1}H, ^{13}C, X-ray, UV, MS	[65,136,137]
98	Neo	–	A	^{1}H, ^{13}C, X-ray	[135]
99	–	–	A	^{1}H, ^{13}C, X-ray	[135]
100	–	–	A	^{1}H, ^{13}C, IR, UV, MS X-ray, CV	[139,140]
102 ($n=3$)	–	–	A	^{1}H, ^{13}C	[141–143]
102 ($n=4$)	–	–	A	^{1}H, ^{13}C	[141–143]
105	–	–	A	^{1}H, ^{13}C	[139]
CCl_2	Mes	Cl	A	^{1}H, ^{13}C, X-ray	[98]
CS_2^{2-} $2K^+$	^{i}Pr	Me	C	^{1}H	[114]
CS_2^{2-} $K^+ \cdot 2THF$	^{i}Pr	Me	C	X-ray	[114]
$C(SMe)_2$	Et	Me	C	^{1}H, ^{13}C	[115]
$C(SMe)_2$	^{i}Pr	Me	C	^{1}H, ^{13}C	[115]
$C(CN)_2$	Et	Me	B	^{1}H, ^{13}C, IR, MS, X-ray	[124]
$C(CN)_2$	^{i}Pr	Me	B	^{1}H, ^{13}C, IR, MS, X-ray	[124]
$C[C(O)Ph]_2$	Me	Me	C	^{1}H, ^{13}C, IR, MS, X-ray	[124]
$SiCl_4$	Me	Me	A	^{1}H, ^{13}C, ^{29}Si	[144]
$SiCl_4$	Et	Me	A	^{1}H, ^{13}C, ^{29}Si, X-ray	[144]
$SiCl_4$	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{29}Si	[144]
$SiMe_2Cl_2$	Et	Me	A	^{1}H, ^{13}C, ^{29}Si	[144]
$SiMe_2Cl_2$	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{29}Si	[144]
$SiPh_2Cl_2$	Et	Me	A	^{1}H, ^{13}C, ^{29}Si	[144]

E	R^1	R^2	Syn	Instrumental analysis	Ref.
$SiPh_2Cl_2$	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{29}Si	[144]
$SiMe_3{}^+I^-$	Et	Me	A	^{1}H, ^{13}C, ^{29}Si	[144]
112 (R^1, R^2 = Neo)			A, C	^{1}H, ^{13}C, ^{29}Si, MS, X-ray	[145,146]
GeI_2	Mes	H	A	^{1}H, ^{13}C, X-ray	[147]
115 (R^1, R^2 = Neo)			A	^{1}H, ^{13}C, MS, X-ray	[146]
$SnPh_2Cl_2$	Me	Me	A	^{1}H, ^{13}C, ^{119}Sn	[144]
$SnPh_2Cl_2$	Et	Me	A	^{1}H, ^{13}C, ^{119}Sn	[144]
$SnPh_2Cl_2$	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{119}Sn, X-ray	[144]
$SnCl_2$	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{119}Sn, X-ray	[144]
Sn(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$	^{i}Pr	Me	A	^{13}C, ^{119}Sn, X-ray	[148]
120 (R^1, R^2 = Neo)	–	–	A	^{1}H, ^{13}C, ^{119}Sn, MS, X-ray	[146]
120 (R^1 = Me, R^2 = $CH_2CH_2NMe_2$)			C	X-ray	[149]
Pb(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$	^{i}Pr	Me	A	X-ray	[150]
123 (R^1, R^2 = neo)			A	^{1}H, ^{13}C, IR, MS, X-ray	[124]
$NNCH_2$	Et	Me	A	^{1}H, ^{13}C, MS	[151]
$NNCPh_2$	Mes	H	A	^{1}H, ^{13}C, IR, MS, X-ray	[152]
$NNC_{13}H_8$ (see **127**)	Mes	H	A	^{1}H, ^{13}C, IR, MS, X-ray	[152]
128	–	–	A	^{1}H, ^{13}C, IR, MS, CV	[47]
NH	Me	H	D	^{1}H, ^{13}C, MS, X-ray, MO	[7,153]
NH	Mes	H	C	^{1}H, ^{13}C, IR, MS	[152]
$NSiMe_3$	Me	H	C	^{1}H, ^{13}C, MS	[153]
PF_5	Mes	H	A	^{1}H, ^{13}C, ^{19}F, ^{31}P	[82]
PF_5	Mes	Cl	A	^{1}H, ^{13}C, ^{19}F, ^{31}P, X-ray	[82]
$PPhF_4$	Mes	H	A	^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P, X-ray	[154]
$POCl_2{}^+Cl^-$	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{31}P	[155]
PO_2Cl	^{i}Pr	Me	C	^{1}H, ^{13}C, ^{31}P, X-ray	[156]
PO_3H	^{i}Pr	Me	C	^{1}H, ^{13}C, ^{31}P, MS, X-ray	[155]
$PPh_2{}^+Cl^-$	Me	H	A	^{1}H, ^{13}C, ^{31}P	[157]
$PPh_2{}^+PF_6{}^-$	Me	H	C	^{1}H, ^{13}C, ^{19}F, ^{31}P	[157]
$PPh_2{}^+Cl^-$	^{i}Pr	Me	A	^{1}H, ^{31}P, MS	[158]
$PPh_2{}^+AlCl_4{}^-$	^{i}Pr	Me	C	^{1}H, ^{13}C, ^{27}Al, ^{31}P, MS, X-ray	[158]
$P(Se)Ph_2{}^+AlCl_4{}^-$	^{i}Pr	Me	C	^{1}H, ^{31}P, ^{77}Se, MS	[158]
PPh_2PdCl_3	^{i}Pr	Me	C	^{1}H, ^{13}C, ^{31}P, X-ray	[159]
PPh_2PtCl_3	^{i}Pr	Me	C	^{1}H, ^{13}C, ^{31}P, ^{195}Pt	[159]
$P(Cl) = NMes^*$	^{i}Pr	Me	A	^{31}P, IR, X-ray	[160]
$P = NMes^{*+}CF_3SO_3{}^-$	^{i}Pr	Me	A	^{19}F, ^{31}P, IR, X-ray	[160]
PCN	Me	–	C	^{1}H, ^{31}P, IR, UV, X-ray	[161]
PCF_3	Mes	H	A	^{1}H, ^{13}C, ^{19}F, ^{31}P, MS, X-ray, MO	[162,166]
PPh	Mes	H	A	^{1}H, ^{13}C, ^{15}N, ^{31}P, X-ray, MO	[162,166]
PPh	Me	Me	A	^{1}H, ^{13}C, ^{15}N, ^{31}P, X-ray, MO	[163,166]
$PPh(BH_3)_2$	Me	Me	C	^{1}H, ^{13}C, ^{15}N, ^{31}P, X-ray	[164]

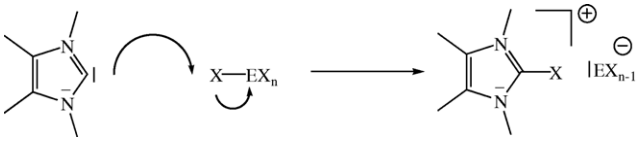
E	R^1	R^2	Syn	Instrumental analysis	Ref.
151	–	–	A	^{1}H, ^{13}C, ^{31}P, MS	[169]
152	–	–	C	^{1}H, ^{13}C, ^{31}P, MS, X-ray	[169]
153	–	–	C	X-ray	[169]
AsF_5	Mes	Cl	A	^{1}H, ^{13}C, ^{19}F, X-ray	[82]
AsPh	Mes	H	A	^{1}H, ^{13}C, MS, X-ray	[162]
AsC_6F_5	Mes	H	A	^{1}H, ^{13}C, ^{19}F, MS, X-ray	[162]
SbF_5	Mes	Cl	A	^{1}H, ^{13}C, ^{19}F, X-ray	[82]
$Sb(CF_3)_3$	Mes	Cl	A	^{1}H, ^{13}C, ^{19}F, X-ray	[170]
O	^{t}Bu	H	A	^{1}H, ^{13}C, ^{17}O, IR, MS, X-ray	[62]
159	–	–	A	^{1}H, ^{13}C, IR, X-ray	[141,143]
160	–	–	A	^{1}H, ^{13}C, IR, X-ray	[141,143]
161	–	–	A	^{1}H, ^{13}C, IR	[143]
162	–	–	A	^{1}H, ^{13}C, IR	[143]
163	–	–	A	^{1}H, ^{13}C, IR, X-ray	[143]
164	–	–	A	^{1}H, ^{13}C, IR, X-ray	[142,143]
165	–	–	A	^{1}H, IR	[139]
S	Me	H	A	^{1}H, X-ray, MO	[7,174]
S	^{t}Bu	H	D	X-ray	[178]
S	Mes	H	A	X-ray	[177]
S	Ad	H	A	X-ray	[177]
S	Fc	H	A	^{1}H, ^{13}C, IR, MS, CV, X-ray	[51]
S	Me	Me	D	^{1}H, ^{13}C, X-ray	[4,196]
S	Et	Me	D	^{1}H, ^{13}C	[4]
S	^{i}Pr	Me	D	^{1}H, ^{13}C	[4]
169 (R^1, R^2 = Bz)	–	–	A	^{1}H, ^{13}C	[120]
69 (R^1 = Me, R^2 = Fc)	–		A, D	^{1}H, ^{13}C, IR, MS, CV	[47]
169 (R^1 = Me, R^2 = CH_2Fc)	–		A	^{1}H, ^{13}C, IR, MS, X-ray	[175]
170	–	–	A	^{1}H, ^{13}C, IR, MS, CV, MO	[176]
SF_2	^{i}Pr	Me	C	^{1}H,^{19}F	[179]
SCl_2	^{i}Pr	Me	A	^{1}H, ^{13}C, MS, X-ray	[179]
$SOCl_2$	^{i}Pr	Me	A	^{1}H, ^{13}C, MS, X-ray	[179]
$S(OMe)Cl_2{}^+I^-$	^{i}Pr	Me	C	^{1}H, ^{13}C	[179]
SO_3	^{i}Pr	Me	B	^{1}H, ^{13}C, IR, MS, X-ray	[182]
$SO_3H^+BF_4{}^-$	^{i}Pr	Me	C	^{1}H, ^{13}C, ^{19}F	[155]
$SO_3H^+SbF_6{}^-$	^{i}Pr	Me	C	X-ray	[155]
Se	Me	H	A	^{1}H, ^{13}C, IR, X-ray	[173]
Se	Me	Me	A	^{1}H, ^{13}C, ^{77}Se	[183]
Se	Et	Me	A	^{1}H, ^{13}C, ^{77}Se	[183]
Se	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{77}Se, X-ray	[183]
177	–	–	A	^{1}H, ^{13}C, IR, MS, CV, MO	[176]
Te	Mes	H	A	^{1}H, ^{13}C, ^{125}Te, X-ray	[98]
Te	Mes	Cl	A	^{1}H, ^{13}C, ^{125}Te	[98]

E	R^1	R^2	Syn	Instrumental analysis	Ref.
Te	Me	Me	A	^{1}H, ^{13}C, ^{125}Te	[184]
Te	Et	Me	A	^{1}H, ^{13}C, ^{125}Te	[184]
Te	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{125}Te, X-ray	[184]
179	–	–	A	^{1}H, ^{13}C, IR, MS, CV, MO	[176]
TeI_2	Et	Me	C	^{1}H, ^{13}C, X-ray	[185]
TeI_2	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{125}Te, X-ray	[186]
$F^+SF_3^-$	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{19}F, X-ray	[179]
$F^+SO_2F^-$	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{19}F, X-ray	[179]
$F^+BF_4^-$	^{i}Pr	Me	C	^{1}H, ^{13}C, ^{19}F	[102]
Cl^+Cl^-	Mes	H	A, B	^{1}H, ^{13}C, IR, MS	[30,94]
Cl^+Cl^-·MeCN	Mes	H	(C)	X-ray	[30]
Cl^+Cl^-	Mes	Cl	A	^{1}H, ^{13}C, X-ray	[98]
Cl^+Cl^-	Me	Me	A	^{1}H, ^{13}C	[24]
Cl^+Cl^-	Et	Me	A	^{1}H, ^{13}C	[24]
Cl^+Cl^-	^{i}Pr	Me	A	^{1}H, ^{13}C, X-ray	[24,99]
$Cl^+Cl{\cdot}H_2O^-$	^{i}Pr	Me	C	^{1}H, X-ray	[24]
$Cl^+SO_2F^-$	^{i}Pr	Me	A	^{1}H, ^{13}C, ^{19}F	[179]
$Cl^+SO_2Cl^-$	^{i}Pr	Me	A, C	^{1}H, ^{13}C, IR, X-ray, MO	[187]
$Cl^+PO_2Cl_2^-$	^{i}Pr	Me	C	^{1}H, ^{13}C, ^{31}P, X-ray	[188]
Cl^+CN^-	^{i}Pr	Me	B	^{1}H, ^{13}C, IR	[105]
$Cl^+Ag(CN)_2^-$	^{i}Pr	Me	B	^{1}H, ^{13}C, IR, X-ray	[105]
$Cl^+AlCl_4^-$	Mes	H	C	^{1}H, ^{13}C, IR, MS, X-ray	[30]
$Cl^+AlCl_4^-$	^{i}Pr	Me	C	^{1}H, ^{13}C,^{27}Al	[24]
$Cl^+1/2TeCl_6^{2-}$	^{i}Pr	Me	C	^{1}H, ^{13}C, X-ray	[189]
Br^+Br^-	Mes	H	A, B	^{1}H, ^{13}C, IR, MS	[30,94]
Br^+Br^-·3 MeCN	Mes	H	(C)	X-ray	[30]
Br^+Br^-	^{i}Pr	Me	A	^{1}H, ^{13}C, X-ray	[190]
$Br^+Br^-{\cdot}CBr_4$	^{i}Pr	Me	C	X-ray	[190]
$Br^+TeBr_5^-$	^{i}Pr	Me	C	^{1}H, ^{13}C, X-ray	[190]
$Br^+1/2TeBr_6^{2-}$	^{i}Pr	Me	C	^{1}H, ^{13}C, X-ray	[189]
I^+I^-	Mes	H	–	X-ray	[191]
I^+I^-	Et	Me	A	^{1}H, X-ray	[192]
I^+I^-	^{i}Pr	Me	A	X-ray	[190]
$I^+I_3^-$	^{i}Pr	Be	A	^{1}H, ^{13}C, X-ray	[193]
187	–	–	A	^{1}H, ^{13}C, X-ray	[27]
$I^+BPh_4^-$	Mes	H	–	^{13}C, X-ray	[191]
I^+CarbI^{-b}	Mes	H	A	^{13}C	[191]
$I^+CarbBPh_4^{-c}$	Mes	H	A	^{1}H, ^{13}C, X-ray	[191]
IC_6F_5	Ad	H	A	^{1}H, ^{13}C, ^{15}N, ^{19}F, X-ray	[194]
189	^{i}Pr	Me	A	^{1}H, ^{13}C, X-ray	[195]

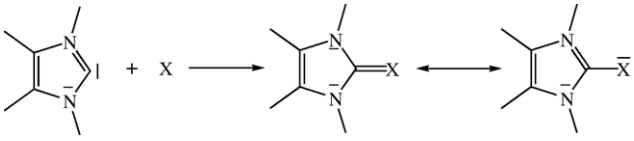
Me = CH_3, Et = C_2H_5, Pr = *n*-C_3H_7, ^{i}Pr = *iso*-C_3H_7, ^{t}Bu = *tert*-C_4H_9, Neo = CH_2CMe_3; Bz = $CH_2C_6H_5$; Fc = $C_5H_4FeC_5H_5$; Ph = C_6H_5, Mes = 2,4,6-$Me_3C_6H_2$, Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$, Isi = 2,6-^{i}Pr$_2$C$_6$H$_3$, Cp* = C_5Me_5; Xyl = 3,5-$Me_2C_6H_3$; Syl = C≡CSiMe$_3$; [b]Carb = **1** (R^1 = Mes, R^2 = H); [c]dimeric in the solid state; [d]Carb = **1** (R^1 = Me, R^2 = H); [e]Carb = **1** (R^1, R^2 = Me); [f]Carb = **1** (R^1 = Isi, R^2 = H); [g]Carb = **1** (R^1 = ^{i}Pr, R^2 = Me).



Scheme 1.



Scheme 2.



Scheme 3.

11. Concluding remarks

Owing to high negative charge density at C2 and the stability of imidazolium ions, 2,3-dihydroimidazol-2-ylidenes react readily with electrophilic centres of most of the main group elements, and form stable adducts. In many cases, those compounds are the first known complexes with neutral ligands for these centres. In general, 2,3-dihydroimidazol-2-ylidenes:

(a) react as strong nucleophiles (Scheme 1);
(b) react as strong reducing agents (X e.g. halogens) or bases (X = H) (Scheme 2); and
(c) exhibit ylidic structures and properties with doubly bound substituents (X e.g. chalcogens, NR, CR_2) at the 2-position (Scheme 3).

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