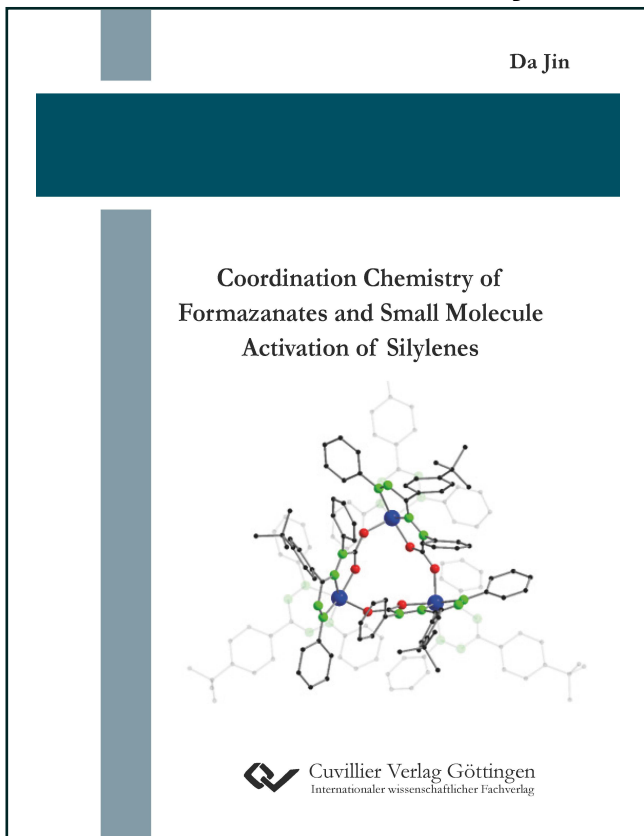




Da Jin (Autor)

Coordination Chemistry of Formazanates and Small Molecule Activation of Silylenes



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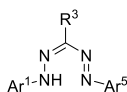
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1. INTRODUCTION

1.1 The coordination chemistry of formazanates

1.1.1 Formazans and formazanates

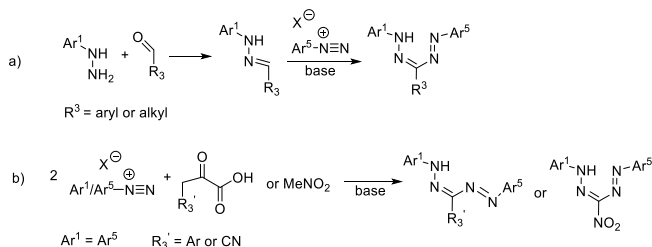
Formazans are known as nitrogen-rich compounds featuring the $-\text{NH}-\text{N}=\text{C}=\text{N}-$ backbone (Figure 1.1.1).¹ They were first reported in the 1890s and have been studied extensively since the 1940s.²⁻⁴ Due to their vivid coloration, these compounds have garnered considerable interest and are often employed as dyes and redox-based staining agents in cell biology.⁵⁻⁸



$\text{R}^3 = \text{aryl, alkyl, CN, NO}_2, \text{ etc}$

Figure 1.1.1. The regular form of formazans.

One of the most attractive features of formazan chemistry is its facile synthesis, which enables the modulation of their properties through structural variation. The most commonly utilized methods for synthesis involve the reaction of aryldiazonium salts with substrates containing activated carbon functionalities (Scheme 1.1.1).⁹⁻¹² For example, triarylformazans and 3-alkyl formazans can be synthesized by coupling an aryl diazonium salt with hydrazones (Scheme 1.1.1, a). This versatile approach allows for the creation of asymmetric formazans with distinct Ar^1 and Ar^5 substituents. Alternatively, symmetric formazans (with $\text{Ar}^1 = \text{Ar}^5$) can be synthesized by coupling two equivalents of aryldiazonium salts with compounds containing activated methylene groups. In this manner, phenylpyruvic acid derivatives can be reacted with two equivalents of aryldiazonium salts to produce triarylformazans, 3-cyanoformazans, and 3-nitroformazans (Scheme 1.1.1, b).



Scheme 1.1.1. Common synthetic routes of formazans.⁹⁻¹²

Formazanates, the deprotonated form of formazans, are similar to the β -diketiminato and dipyrinate classes of ligands but have unique electronic properties, including the presence of high-lying filled (e^- donor) and low-lying empty (e^- acceptor) orbitals of π -symmetry (Figure 1.1.2).^{13,14} Both of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in formazanate ligands consist primarily of orbitals centered on the [NNCNN] backbone, with additional contributions from the π -conjugated aromatic $N-Ar^1/Ar^5$ groups. Compared to other chelating N-donor ligands, the LUMO of formazanates is lower in energy, which makes compounds containing these ligands more likely to engage in ligand-based reduction reactions.

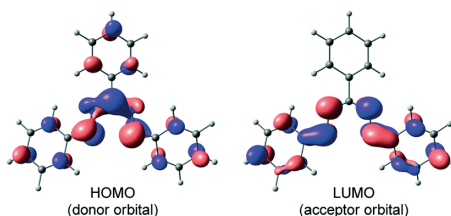


Figure 1.1.2. Frontier (Kohn-Sham) orbitals of the triphenylformazanate anion in the commonly observed ‘closed’ form, calculated using density functional theory (B3LYP/6-31G(d)).¹⁵

The presence of four nitrogen atoms in the framework confers coordination flexibility, allowing the formation of four-, five- and six-membered chelates, corresponding to “linear”, “open” and “closed” modes of the formazanate ligand (Figure 1.1.3).^{16,17} When adopting a symmetric coordination mode, characterized as “linear” and “closed” chelating rings, the bond lengths in the backbone are often intermediate between single and double bonds, suggesting high electron delocalization within the π electron system. Conversely, in the case of the five-membered “open” mode chelate ring, the bond parameters usually exhibit clear alternation between single and double bonds.

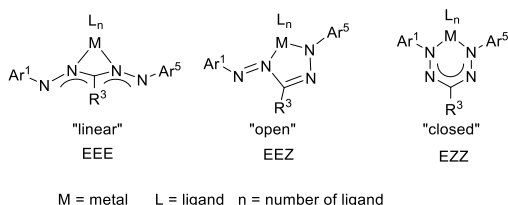
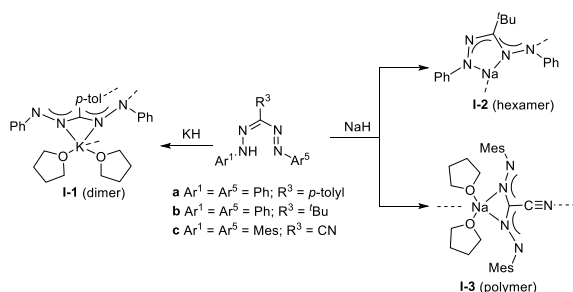


Figure 1.1.3. Common coordination modes of formazanate ligands in complexes.^{16,17}

The convenient synthesis of formazans and formazanates, coupled with their exceptional properties, has sparked a renewed interest in their coordination chemistry. Both main group elements and transition metals have been investigated in formazanates chemistry.

1.1.2 Formazanates with main group compounds

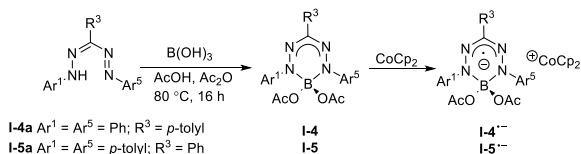
The successful synthesis of alkali metal formazanate salts provides a promising avenue for their use in salt metathesis reactions. The salts were obtained by deprotonation of the neutral formazans with strong alkali metal bases [NaH] and [KH] (Scheme 1.1.2).¹⁸ Due to the availability of both internal and terminal nitrogen atoms in the [NNCNN] backbone, formazanates exhibit diverse coordination chemistry. The potassium salt [K(PhNNC(*p*-tol)NNPh)(thf)₂] (**I-1**) displays a unique dimeric structure through the bridging interaction of the potassium ion with a terminal nitrogen atom and the aromatic ring of a second unit. In contrast to the dimeric structure, the compounds [Na(PhNNC(^{*t*}Bu)NNPh)] (**I-2**) and [Na(MesNNC(CN)NNMes)(thf)₂] (**I-3**) exhibit hexameric and polymeric structures in the solid state, respectively. The alkali metal in these compounds binds to the formazanate ligand through internal nitrogen atoms or both internal and external nitrogen atoms, resulting in the formation of different chelate geometries.



Scheme 1.1.2. Synthesis of formazanate alkali metal salts.¹⁸

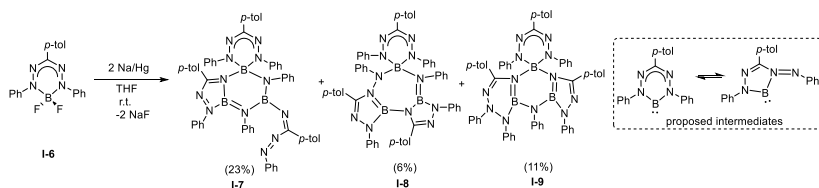
The adducts of four-coordinated boron complexes have been the most extensively studied family of formazanate coordination compounds over the past two decades.^{15,19-21} In 2007, Hicks and co-workers sparked interest in a novel class of molecular materials by converting triarylformazans to boron diacetato complexes of formazanate ligands.¹⁹ Their work demonstrated that these complexes could be reduced into stable verdazyl-type radical anions, which could be identified in the solid state by using UV-Vis absorption and EPR spectroscopy

(Scheme 1.1.3). This work was the first demonstration of formazanates as redox-active ligands and such discovery laid the foundation for subsequent researches. After that, formazanate boron difluoride complexes were synthesized, which were structurally rigid and stable due to the BF_2^{+} fragment.²⁰ These complexes could be further reduced by $[\text{CoCp}_2]$, yielding the first structurally characterized examples of radical anions supported by formazanates. These radical anions were observed to exhibit characteristic elongation of the formazanate N–N bonds, with an average increase from approximately 1.309 Å for the neutral form to 1.362 Å.



Scheme 1.1.3. Synthesis of formazanate boron compounds and their radical anions.¹⁹

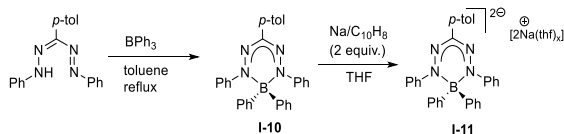
Generating the dianion form of BF_2 formazanates remains a challenge due to the limited number of reducing agents that possess sufficient strength to accomplish this feat. The Na/Hg amalgam was employed in an attempt to isolate the dianion form of BF_2 formazanates (Scheme 1.1.4).²¹ The treatment of formazanate BF_2 complex with two equiv. of Na/Hg led to the production of novel, crystallographically-characterized BN heterocycles (**I-7-9**). This formation of BN heterocycles was attributed to the production of $[\text{NaF}]$ and likely involved B(I) carbenoid intermediates.



Scheme 1.1.4. Treatment of formazanate BF_2 with Na/Hg amalgam.²¹

The lack of effective methods to advance the two-electron reactivity of redox-active formazanate ligands has been a significant obstacle in this field. To overcome this challenge, researchers have investigated boron diphenyl (BPh_2) formazanates as potential candidates.²² The absence of boron-halide bonds in their framework offers promise in circumventing the formation of salts, which had previously complicated the redox reactivity of BF_2 formazanates.

The synthesis of formazanate BPh₂ complex (**I-10**) was accomplished by refluxing BPh₃ with the appropriate formazan in toluene. Further treatment with two equiv. of Na/C₁₀H₈ led to the successful generation of the radical dianion (Scheme 1.1.5). This work has produced the first-ever dianion of a formazanate complex, which marks a significant step forward in enabling further reactivity studies.

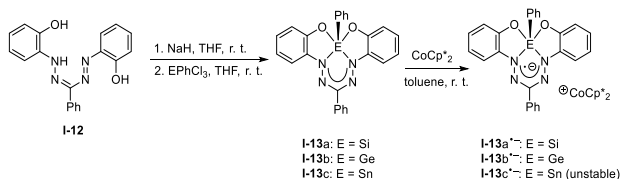


Scheme 1.1.5. The synthesis of formazanate BPh₂ complex (**I-10**) and its radical dianion (**I-11**).²²

Despite the extensive research on boron formazanate complexes, their heavier group 13 analogues have received relatively little attention. The Sundermeyer group synthesized the first heavy group 13 complexes of formazanates by reacting MMe₃ (M = Al, Ga, In) with a triarylformazan in toluene.²³ These complexes exhibited low-energy absorption maxima and large molar extinction coefficients. Although preliminary cyclic voltammetry (CV) studies indicated that the complexes could not be reversibly oxidized or reduced, further investigations are needed to shed light on their electrochemical properties. Mondol and Otten conducted a recent study that expanded the structural diversity of aluminum formazanate complexes significantly.²⁴ They isolated the first examples of ligand-supported radical anions and dianions derived from aluminum formazanates *via* the treatment of formazanate diphenyl aluminum complex with [CoCp₂] or Na/Hg amalgam.

For group 14 elements, the first and only formazanate complexes featuring hypervalent (5-coordinate) group 14 atoms were reported in 2018.²⁵ These complexes were prepared by reacting the trianion of 1,5-bis(2-hydroxyphenyl)-3-phenylformazan with the respective phenyl trichlorides of Si, Ge, and Sn (EPhCl₃) in THF (Scheme 1.1.6). Unlike related high-valent group 14 complexes of bipyridine N₂O₂ ligands that adopt a trigonal bipyramidal geometry,²⁶ the formazanate complexes adopt a distorted square-pyramidal geometry, which is crucial when considering their possible conversion to the corresponding radical anions. Chemical reduction with [CoCp*₂] led to stable radicals containing Si and Ge, while Sn-containing radicals could not be isolated due to irreversible reduction events at more negative potentials. The planarity deviation of the π -electron systems of formazanate complexes of Si, Ge, and Sn

increased with atomic size, and this trend was linked to the lower stability of the Sn-containing radical anions. The stability of these stable radicals without significant steric bulk demonstrated the critical role of structural planarity and π -electron delocalization in stabilizing radical species.

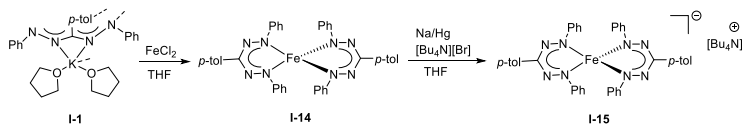


Scheme 1.1.6. Synthesis of group 14 complexes supported by formazanate ligands.²⁵

1.1.3 Formazanate with transition metal compounds

In transition metal formazanate complexes, the d-orbitals interact strongly with the π^* -orbital of the adjacent ligand, resulting in a high degree of metal-ligand bond covalency through π -backdonation. This covalency leads to the manifestation of unusual electronic and magnetic properties such as spin-crossover and valence tautomerism.

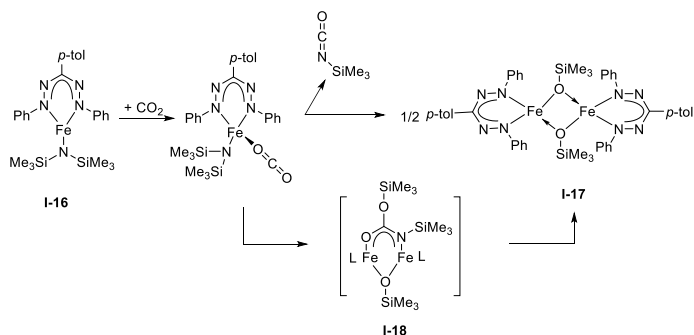
Among formazanate transition metal complexes, there is a greater emphasis on researching Fe element compared to other transition metals. In 2016, a study was published detailing the synthesis of the Fe(II) complex using the simple [FeCl₂] *via* salt metathesis with potassium formazanate (Scheme 1.1.7).²⁷ Crystallographic analysis of the resulting complex revealed a flattened tetrahedral structure with remarkably short Fe–N bond lengths. The NMR and UV/Vis spectra indicated a temperature-dependent equilibrium between a diamagnetic state ($S = 0$) at low temperature and a paramagnetic state ($S = 2$) at high temperature. The occurrence of spin-crossover in a four-coordinated complex was found to be unusual and attributed to π -backdonation from the d_6 metal center to a low-lying formazanate π^* -orbital. The one-electron reduction of bis(formazanate) Fe with one equiv. of Na/Hg as the reducing agent yielded a high-yield synthesis of the anionic, which is a low-spin ($S = 1/2$) Fe(I) complex with closed-shell, monoanionic formazanate ligands. Even though ligand-based reductions are common for these 'redox-active' ligands, the empirical data do not support an alternative description in which reduction occurs at the ligand with the additional electron in the low-energy formazanate π^* -orbital.



Scheme 1.1.7. Synthesis of bis(formazanate) iron(II) complex and its reduction product.²⁷

Furthermore, the Holland group investigated the redox-active nature of the formazanate Fe(II) complexes by preparing the one-electron reduction product using mono-formazanate iron amide and its THF adduct.^{28,29} Calculations suggested that the reduction product could exist in two dominant configurations, one as a high-spin Fe(II) center anti-ferromagnetically coupled to a singly occupied ligand π^* -orbital and the other as a high-spin Fe(I) center without ligand participation. Besides, the effect of the counter cation on the structure of formazanate Fe(II) was also examined. The compounds were shown to be dimeric in the solid state when the counter cation was one of the alkali metals (Na^+ , K^+ , Rb^+ or Cs^+), but formed monomeric species in solution when the alkali cation was sequestered with crown ether or allowed to equilibrate in THF solution.

The reaction of the neutral formazanate Fe(II) complex or its thf-adduct towards CO_2 was also subsequently explored by the same group in 2018 (Scheme 1.1.9).³⁰ It was shown to cleanly form isocyanate and the dimeric iron siloxide product *via* the carbamate intermediate, which was isolated and crystallographically characterized. This is the only example of CO_2 activation by formazanate complexes.

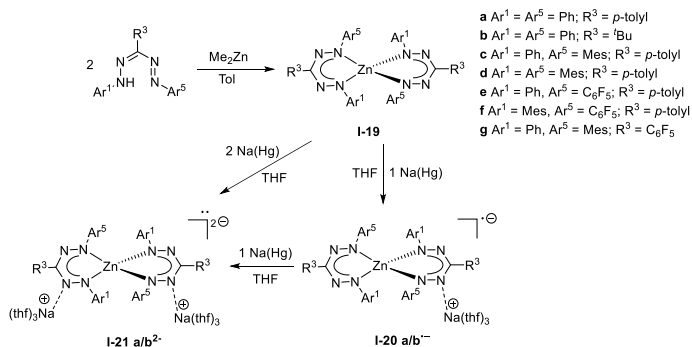


Scheme 1.1.9. Reaction of CO_2 with the mono(formazanate)iron(II) complex.³⁰

Apart from the formazanate Fe complexes, the chemistry of Ni and Zn complexes supported by formazanate ligand is also well established. Reports published since 2000 have significantly

expanded our understanding of nickel complexes with formazanate ligands. Notably, in 2006, the group of Vatsadze confirmed the previously known bis-(triphenylformazanate)nickel complex³¹ to possess a symmetrical, six-membered chelate structure.³² Further investigations have explored the effects of ligand substituents on the spectroscopic and electrochemical properties of related nickel complexes. Tezcan and colleagues prepared derivatives of nickel complexes with pyridine substituents on the formazanate backbone, which were intended for use as potential metalloligands in supramolecular chemistry.³³ In a similar vein, Zaidman and co-workers prepared a series of bis(formazanate) nickel complexes using formazans with various (hetero)aromatic substituents or linked bis-formazan scaffolds.³⁴ These complexes were investigated for their catalytic activity in ethylene oligomerization, which showed promise but also resulted in substantial amounts of (poly)ethyltoluenes due to Friedel–Crafts alkylation of the toluene solvent with ethylene.

Recent reports have also focused on the properties of formazanate zinc complexes, particularly their ability as redox-active ligands, or electron-reservoirs. In 2014, bis(formazanate) zinc complexes and their corresponding radical anions were synthesized by Otten group (Scheme 1.1.10).³⁵ In these radical anionic complexes, the two formazanate ligands around the zinc center were found to be different, with one having intra-ligand metrical parameters similar to the starting materials, and the other ligand showing substantially elongated N-N bonds, indicating the presence of a radical dianion in the metallaverdazyl form. Treatment of one more equiv. of Na/Hg with radical anionic complexes resulted in the formation of the corresponding dianionic complexes, the first examples of diradical “metallaverdazyl” compounds. The same group also investigated the influence of substitutions on the resulting bis(formazanate) zinc complexes.³⁶ The majority of the formazanate Zn compounds commonly exist in a six-membered chelate ring, but when the N-aryl substituents are electronically non-equivalent, five-membered chelate rings become accessible. Despite the limited stability of these highly reduced species, it is noteworthy that five different oxidation states are accessible in these simple compounds as observed in the voltammograms and this suggests that each formazanate ligand can be reduced by up to two electrons.



Scheme 1.1.10. Synthesis of bis(formazanate) Zn complexes.^{35,36}

1.2 Silylenes and their reactivity towards C–O multiple bonds

1.2.1 Isolable silylenes

Silylenes are divalent silicon species that play an important role as reaction intermediates in silicon chemistry. They are analogous to carbenes in organic chemistry. While carbenes can exist in either triplet or singlet ground states, silylenes tend to adopt the $(3s)^2(3p)^2$ valence electron configuration due to the Si atom's inherent resistance to s , p -orbital hybridization.^{37,38} Like carbenes, silylenes are highly reactive and have been a subject of intense study over the years.³⁹⁻⁴² In the 1980s, several organosilylenes were isolated and characterized in argon or hydrocarbon matrixes, typically at very low temperatures (77 K or below).⁴³ At higher temperatures, they rapidly react with solvents or dimerize or further polymerize with themselves.

Even though silylenes are highly reactive and often unstable, recent advancements in stabilization strategies have led to the discovery of a wide variety of stable and isolable silylenes. Figure 1.2.1 showcases some of the representative isolable silylenes that have been reported. The first isolable silylene, **A**, was synthesized by Jutzi and co-workers in 1986, using the reduction of dibromobis(pentamethylcyclopentadienyl)silane with anthracene-potassium.⁴⁴ However, due to the supercoordinated nature of the silicon center, it cannot be considered as a dicoordinated silylene species. The first isolable dicoordinate silylene *N*-heterocyclic silylene **B** was reported by Denk and West, *et al.*,⁴⁵ and is considered to be congeners of Arduengo's carbenes.⁴⁶ The silicon atom is stabilized by two π -donating amino

groups and a bulky *tert*-butyl substituent. Additionally, the overall 6π electron aromatic character provides additional stabilization. In 1999, Kira *et al.*⁴⁷ succeeded in isolating dialkylsilylene **C** for the first time, using the bidentate ligand 1,1,4,4-tetrakis(trimethylsilyl)butane-1,4-diyl to prevent dimerization. This special silylene is stereostabilized and has the least electronic perturbation compared to other previously known silylenes.

In 2006, two research groups made significant contributions to the field of N-heterocyclic silylenes. Driess *et al.*⁴⁸ reported the synthesis of the first six-membered NHSi (**D**) supported by a modified β -diketiminato (Nacnac) backbone. The compound was synthesized through the reduction of the dibromosilane with $[KC_8]$. In a parallel development, Roesky *et al.* reported the first example of a four-membered NHSi compound in the form of a chlorosilylene stabilized by an amidinato ligand $[L^PhSiCl]$ ($L^Ph = PhC(N^tBu)_2$, **E**).⁴⁹ Although it was initially prepared in 10% yield by reducing the corresponding trichlorosilane $[L^PhSiCl_3]$ with potassium, in 2010, the same group published an alternative high-yield route by dehydrochlorination of $[L^PhSiHCl_2]$ with either $[LiN(SiMe_3)_2]$ or NHC (1,3-di-*tert*-butylimidazol-2-ylidene).⁵⁰

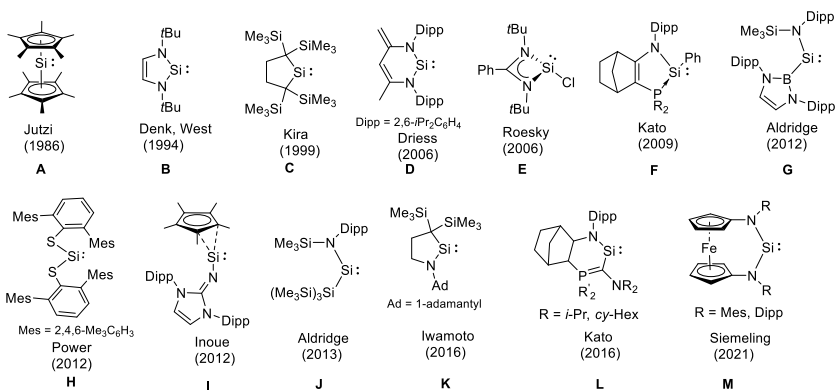


Figure 1.2.1. Selected isolable silylenes.

In 2009, Kato *et al.* reported the first isolable phosphonium silylene **F**, which was synthesized by reacting racemic 2-phosphinoenamine with an equivalent amount of magnesium.⁵¹ The isolable acyclic dicoordinate silylenes **G–J** were subsequently synthesized by Aldridge,⁵² Power⁵³ and Inoue⁵⁴ groups in 2012–2013. The silylene **G** with a boryl substituent was obtained by reacting the tribromo(amino)silane with two equivalents of the boryllithium reagent. The presence of the boryl group, which is an electropositive σ -donor, and the relatively wider N–