APPLICATION OF α, β -UNSATURATED FISCHER CARBENE COMPLEXES FOR SYNTHESIS OF HETEROCYCLIC COMPOUNDS

Abstract

Group 6 metal carbene complexes, especially Fisher carbene complexes, can combine with different nitrogen-containing compounds to generate different monoheterocyclic and polyheterocyclic products. Generally, polyheterocyclic rings can be processed in one step with high selection. Among these, simple nitrogen heterocycle formation appears to be feasible both mechanically and synthetically.

Keywords: Fischer Carbene Complexes, Dotz Benzanullation, Heterocycles, Cycloaddition, Benzannulation.

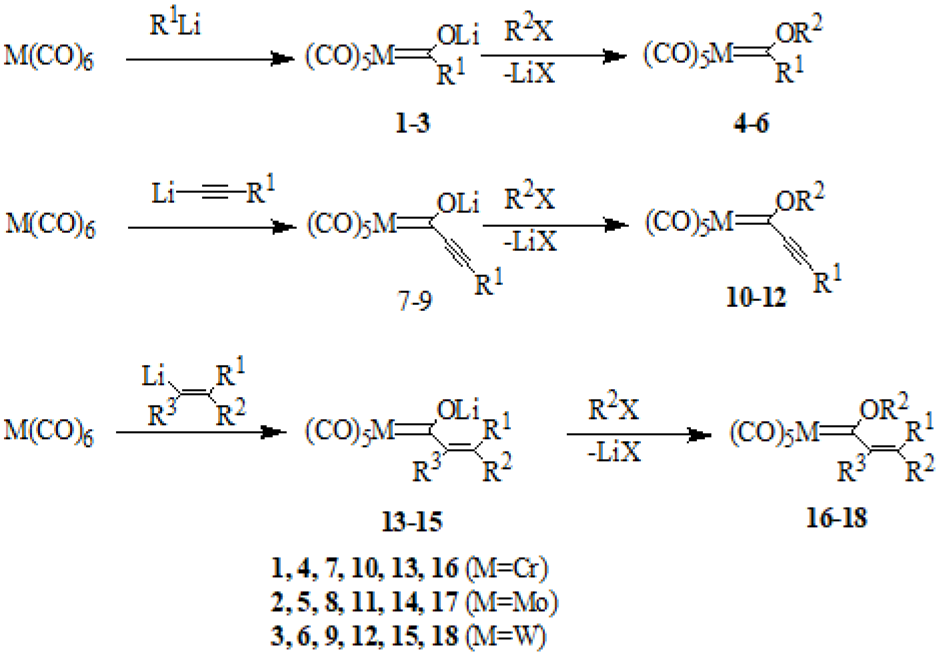
Author

Priyabrata Roy
Department of Chemistry
Victoria Institution (College)
Kolkata, India.

I. INTRODUCTION

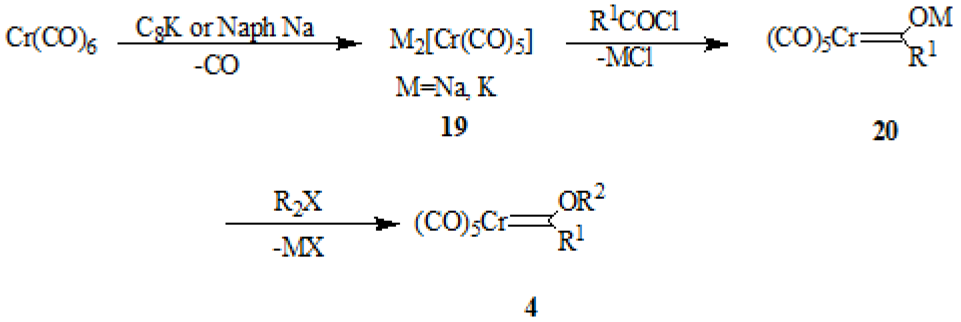
Combinations of carbenes and organometallic moieties form carbene complexes. These are mainly divided into Fischer-type complex and Schrock-type complex. The role of Schrock-type complexes (initially identified in 1970) in olefin metathesis (2005 Nobel Prize winner[1]) is very important. On the other hand, Fischer carbene complexes (FCC), discovered in 1964[2a] and 1965[2b], were developed as powerful organic synthesis reagents[3]. This chapter focuses on the synthesis of azaheterocycles using Fischer carbene complexes, with special focus on chromium complexes, which are the most important of the Fischer carbenes due to their balance of coordination and safety and ease of possession (see below) and widest usage area.

1. **Synthesis of Fischer Carbene Complexes (FCC):** Addition of carbon nucleophile and carbon electrophile to the metal-coordinated carbon monoxide ligand (Scheme 1.1) is the first and most common approach to Fisher-type metal carbenes ("Fisher route").[4] Noble metal salts 1-3, 7-9 and 13-15, respectively, can be generated by adding organolithium reagents (alkyl-, aryl-, alkenyl- or alkynyl lithium derivatives) to chromium hexacarbonyl. and can be alkylated[5a,b] in situ by treatment with as trialkyloxonium tetrafluoroborates[5a,b] or alkyl fluorosulfonates[5c-e] to form alkoxy carbene complexes 4-6, 10-12, 16-18 respectively in moderate yield. Nobel metal salts can also be alkylated by methyl iodide in presence of phase transfer catalyst.[6]



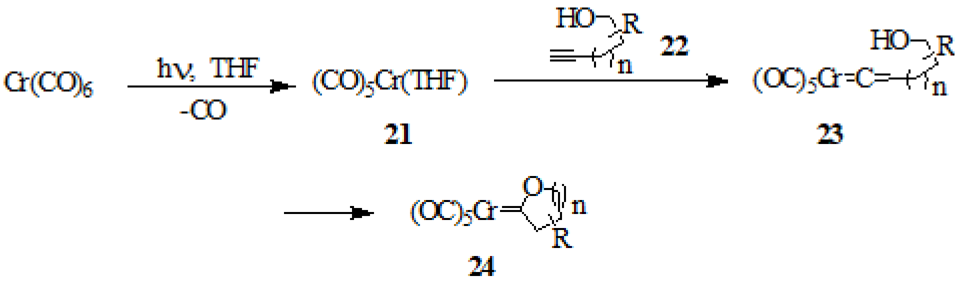
Scheme 1.1

An important limitation of the Fisher method may be the presence of organolithium compounds. Here, the addition of alkoxycarbene complexes (Semmelhack-Hegedus method) provides another route, which involves addition of pentacarbonylchromate dianion 19 (obtained by reduction of hexacarbonylchromium) with sodium naphthalene (NaphNa)[8a,b] or the simply C8K[8C] to acyl chlorides (Section 1.2)[7,8]. Alkylation of acylchromate 20 gives alkoxycarbene complex 4. Both Fischer and Semmelhack-Hegedus methods were used for the synthesis of dicarbene[10a] and multimetallic carbene complexes[10b].



Scheme 1.2

Finally, a specific synthesis method for cyclic carbene complexes was developed (Scheme 1.3). In the presence of weak ligands (such as tetrahydrofuran[11a] or triethylamine[11b]), one of the carbonyl ligands in chromium hexacarbonyl undergoes photochemical cleavage to form the chromium pentacarbonyl σ-complex $(OC)_5CrL$ 21, which reacts with omega-alkynols 22[12,13]. In this case, firstly the vinylidene complex (23) (which can be formed with[12a-f] or without[12g] irradiation) is generated and then converted into metal oxacycloalkylenes (24).



Scheme 1.3

Generally, water, air and diluted acids or bases cannot react with Fischer carbene complexes. They have high dipole moment (4-5 Debye). Though, they can be purified by column chromatography using eluent petroleum ether through silica gel and can be identified by seeing their colour. The Fischer carbene complexes containing OMe or any other alkoxy group as stabilizing group is generally related to the carbon substituents' hybridization present in the carbene carbon. Carbons with sp^3 hybridization are generally yellow in colour, carbons with sp^2 hybridization are generally red in colour and Carbons with sp hyridisation are generally black/dark purpe in colour (Figure 1.1).[13]

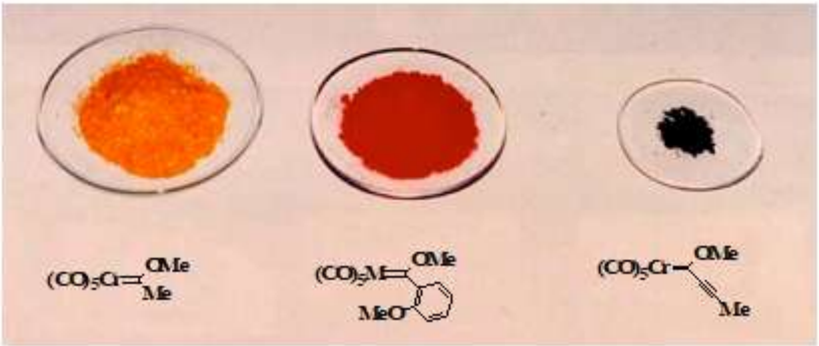
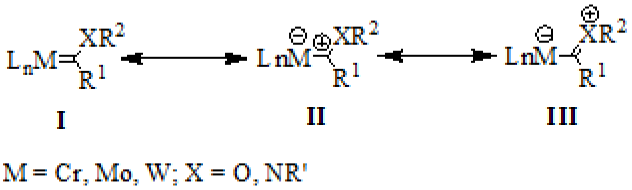


Figure 1.1

- **General reactions:** Generally group 6–8 transition metals form Fischer Carbene Complexes. In the organometallic fragment they have low oxidation state and attached with a ligand with good pi-acceptor (usually CO).

The carbon atom of the FCC signifies a strong electron loving epicenter with a upfield refraction carbon NMR shift near 400 ppm,[14] similar to carbocations (see mesostructure II in Fig. 1.2), mainly due to the π of nitrogen or oxygen (i.e. heteroatoms) resulting in stabilization as shown in mesoscopic model III. Therefore, the metal carbonyl fragment acts as a functional part that trigger the ligand of the FCC for the corresponding reaction. The characteristic reaction structures of carbonylalkylcarbene complexes are shown in Figure 1.3. The Carbene carbon atoms' electrophilic nature promotes the attack by electron rich carbon and heteroatom (pathway A). Electrophile can be added to the carbene heteroatom substitution (path B), that presents the initial stage in the production of metal carbyne from metal carbene.[15,16]

Due to the electron loving property of the carbene carbon, the P^H of the α-CH group decreases. For example, the pKa of methoxy (methyl) carbene chromium complex 4 (R1 = R2 = Me) is ~8.[17] Deprotonation of a strong base therefore produces a metal carbene anion that can be used as a C-nucleophile in alkylations, aldol reactions and Michael-type reactions (path c).



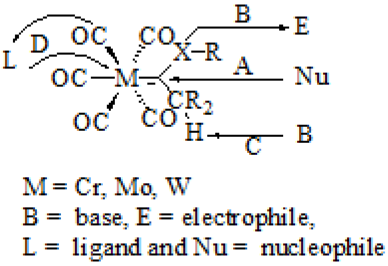
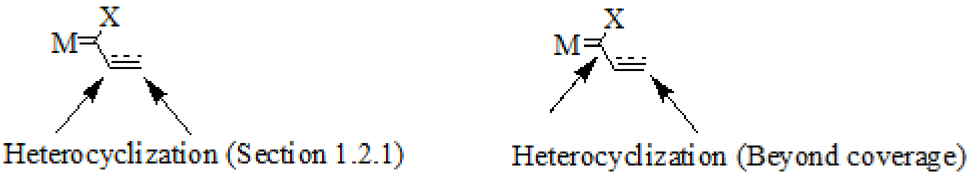


Figure 1.2

Figure 1.3

At last, carbonyl ligand goes through either photochemical or thermal substitution of other ligand species (e.g., phosphine, alkene, alkyne), thus allowing the transformation of modified ligand spheres (method d). These reaction models indicate that organometallic functional groups can be undergo through ligand-centered or metal-centered reactions. Another type of reaction of carbene complexes is the addition of metal-carbene bonds (intramolecular) to the C-H bond used for heterocyclic compound synthesis: ortho-phenyl (dialkyl amino) Cr(0) carbene complexes are converted to indole. Yield is 70. -80% at room temperature.[18] An zero metal site generates after decarbonylation in the sphere of the co-ligand. it can act as a template and can provide the blueprint for subsequent synthesis, allowing the Carbon–Carbon bond generation in the metal co-ordination sphere.[19,20]

2. **Aza-heterocycles Synthesis:** The metal carbenes' function in the generation of the cyclic structure (Figure 1.4) can be divided into two parts. Heterocyclic ring formation reactions in which the carbon atom of the FCC with α,β-unsaturation does not directly partake, though the C-α and C-β carbon atoms partake (Section 1.2.1). Methods for the Synthesis of aza-heterocycles using the specific reaction of FCC are not covered here.



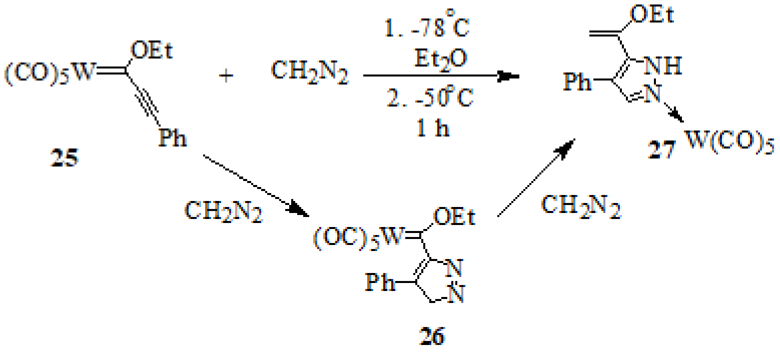
Heterocyclization (Section 1.2.1)
Heterocyclization (Beyond coverage)

Figure 1.4

3. Synthesis of Heterocycles involving Unsaturated Carbene Complexes C–C π-bond

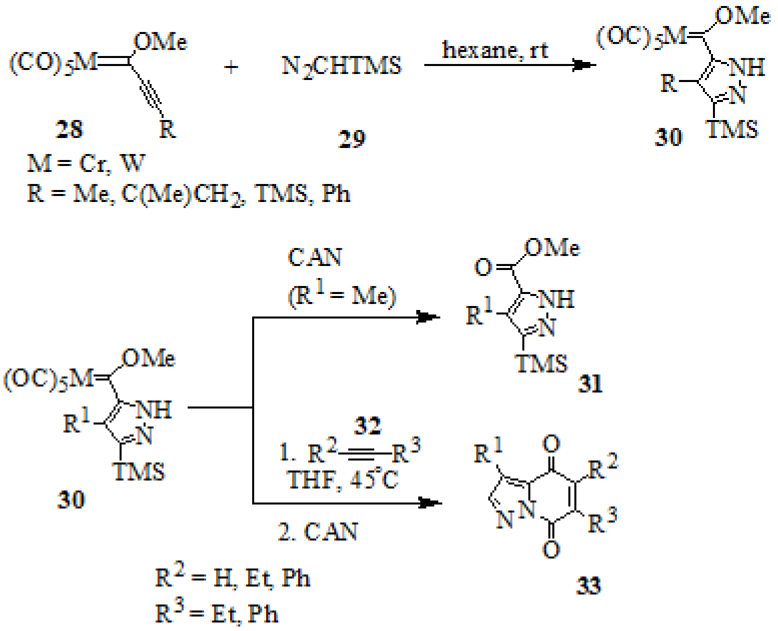
Heterocycles: Five-membered: The metal pentacarbonyl part is a strong electrophile, leaving the alternative π system very electron deficient. Another interesting fact is that afterwards the necessary reactions have occurred, the products of the reactions still holds the carbene metal functionalization necessary for successive operations. Carbonucleophile and heteronucleophile reagents go through Michael-type addition has been evaluated enormously. In addition, [4+2] cycloaddition between traditional carbadienes and Group 6 α,β-unsaturated carbene complexes are exemplified many times. In comparison, only few reports are available of 1,3-dipolar cycloaddition of the FCC containing α,β-unsaturation.[21] Diazomethane derivative, nitrilimine and nitron have been effectively used as dipole with unsaturated FCC. Synthesis of nitrogen heterocycles through cycloaddition reaction between nitrilimines and diazomethane dipoles have been described here.

Tungsten phenylethynyl-ethoxy-carbene complex 25 reacts with diazomethane to give pyrazole derivatives 27 (Scheme 1.4).[22] This is a cycloaddition reaction discovered by Fischer in 1973. The reaction goes through intermediate 26 (not recovered). Then another molecule diazomethane reacts with the produced carbene functionality and produce the pyrazole ring.



Scheme 1.4

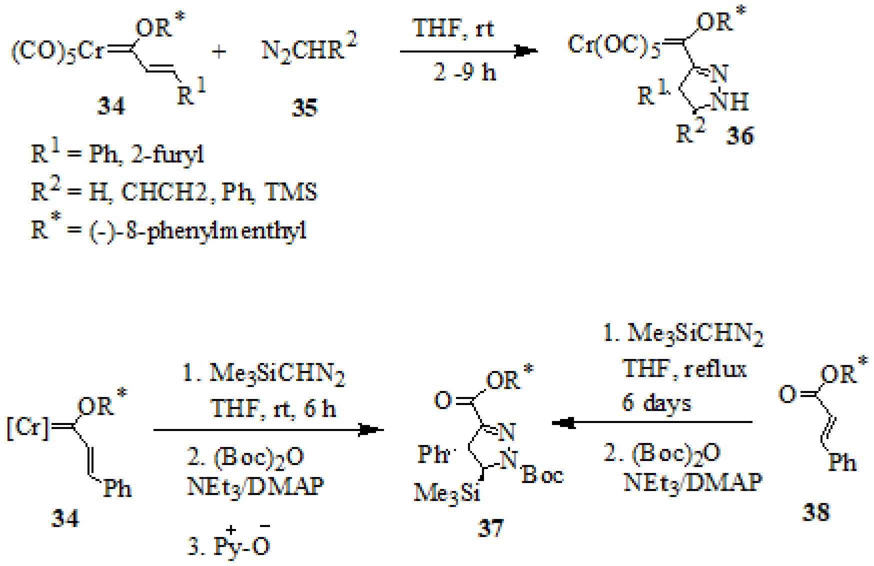
Ten years later, Chan and Wulff examined this phenomenon in more detail (Chapter 5).[23] Therefore, the cycloaddition reaction of alkynylcarbene complex 28 with trimethylsilyldiazomethane 29 occurs at room temperature, forming the pyrazole ring systems 30 in high yield and full regioselectivity. Carbene group metals (M = Cr, W) can be efficiently oxidized by ceric ammonium nitrate (CAN) to pyrazole esters (31). Furthermore, the new alkenylcarbene complex (30) undergoes a benzocyclization reaction with an alkyne (32) to yield moderately synthetic pyrazole (33) in low to moderate yield. Interestingly, the cyclization reaction involves the conjugated carbon-nitrogen double bond of 30 tautomers instead of the carbon-carbon double bond.



Scheme 1.5

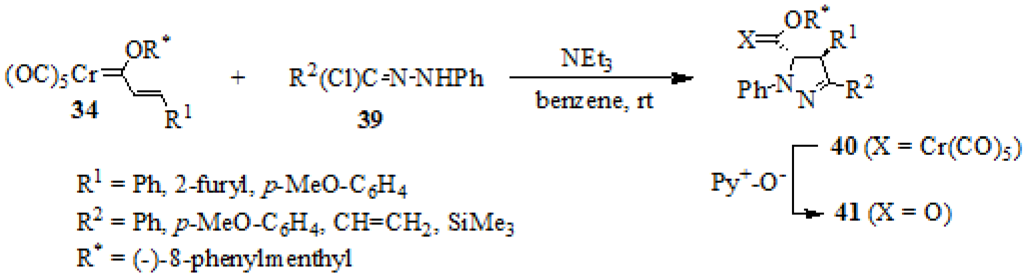
A few years later, Maiorana and co-workers showed that alkenyl(alkoxy) chromium carbene complexes could undergo 1,3−dipolar cycloaddition between diazomethane and trimethylsilyl diazomethane to yield pyrazolines.[24] This dipolar cycloaddition reaction was studied in more detail by Barluenga and co-workers (Scheme

1.6) later.[25,26] Accordingly, FCC derived from (-)-8-phenyl-menthol 34 were reacted with different diazo compounds 35 at normal temperature to obtain diastereoselective pyrazolyl carbene complexes **36** in moderate yields. Dipolar cycloaddition methods for the preparation of pyrazolines (37) using metal alkenyl carbenes (34) or alkenyl esters (38) were compared and the outcomes are summarized in the scheme. Though the preparation of pyrazoline 37 from complex 34 requires an additional step from ester 38 (oxidation of pyridine to carbonyl of the metal carbene), the chemical yield, reactivity and diastereo-selectivity efficiency are undoubtedly higher in the previous case.



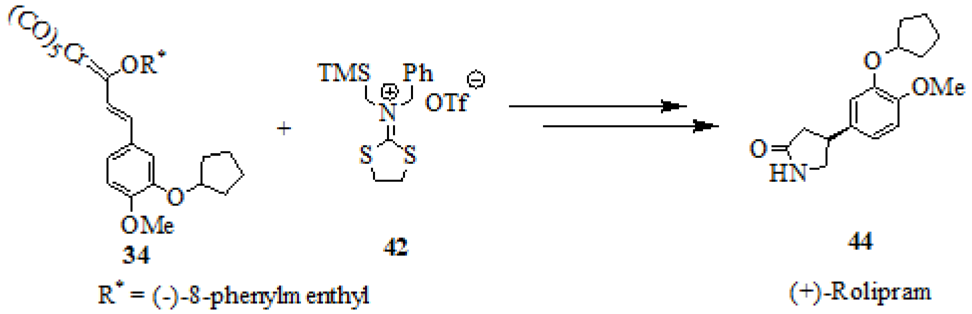
Scheme 1.6

Similarly, many imines formed from chlorohydrazone 39 and NEt3 react smoothly with the chromium carbene complex 34 to form N-phenylpyrazoline derivative 40, which is further oxidized to the nonmetallic pyrazolines (Scheme 1.7) with pyridine oxide. The overall efficiency is high and the diastereoselectivity is very good.[27]



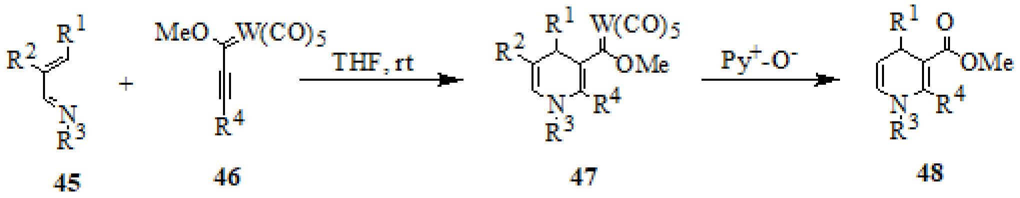
Scheme 1.7

Based on this concept, short-term, high-yield and diastereoselective synthesis of the anti-inflammatory and antidepressant drug (+)-rolipram has recently been achieved (Section 1.8).[28] The main step involves the dipolar cycloaddition of the enantipure chromium carbene complex 34 with the imine ylide dipole 42, thus obtaining rolipram 44 as the single enantiomer in an overall yield of 28%.



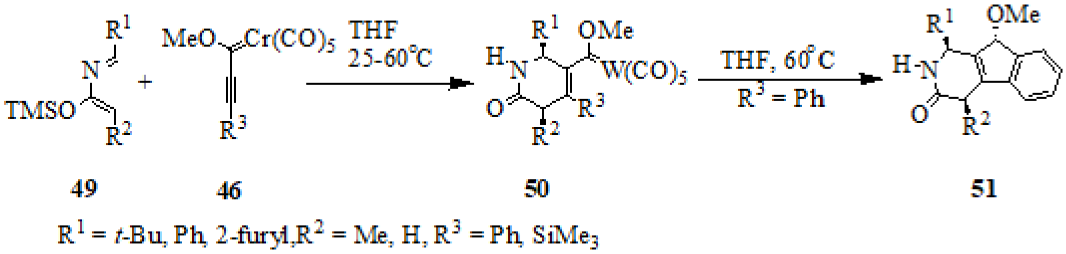
Scheme 1.8

6-Membered aza-heterocyclic rings can be easily obtained through the [4+2] cycloaddition reaction of metal carbenes. So, 1-aza-1,3-diene 45 is neatly cycloadditioned to tungsten alkynylcarbene 46 to give the 1,4-dihydropyridine complex 47 in good yield (Scheme 1.9). An example of oxidation by pyridine oxide from 47 to the ester 48 has also been stated.[29]



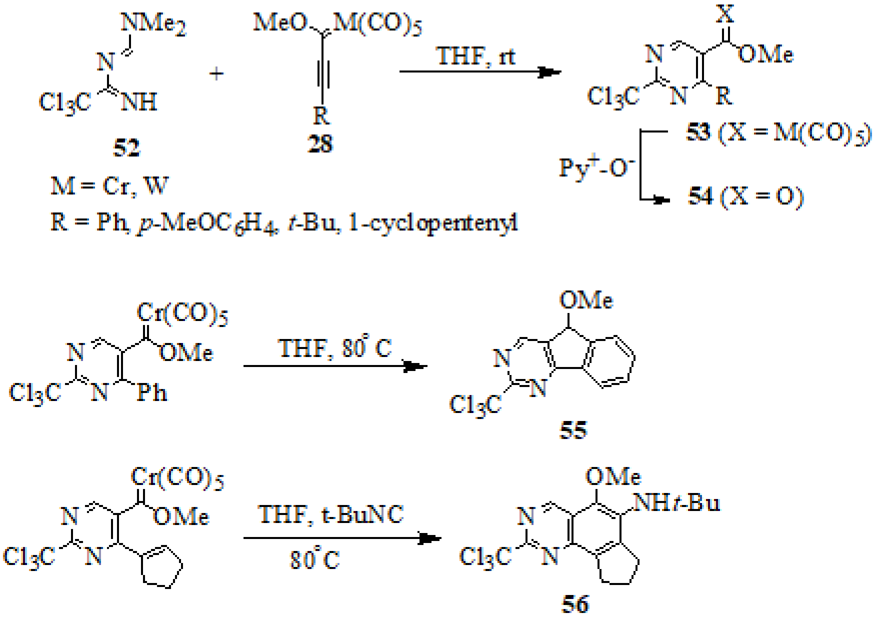
Scheme 1.9

Similarly, heterodiene 49 was incorporated into the dihydropyridone skeleton (Scheme 1.10).[30] Therefore, cycloaddition of alkynylcarbene 46 and 2-azadiene 49 occurs at room temperature (for R1 = 2-furyl) or 60°C (for R1 = 2-furyl) to form pyridone complex 50. This can be isolated when R^1 = t-Bu. This allows thermal conversion to the metal-free heterocycle 51. The formation of 2-azafluorenone 51 is well explained by metalloelectrocycle closure and reductive metal elimination 50 (for R3 = Ph).



Scheme 1.10

The [4+2] cycloaddition strategy has also been used for the synthesis of pyrimidine rings (Scheme 1.11).[31] Therefore, treatment of complex 28 with diazadiene species 52 leads to the formation of pyrimidine carbene complex 53, which is oxidized to pyrimidine ester 54. The chromium carbene adduct can be thermally converted to polyheterocycle 55 (see Formation 51, Scheme 1.10) or by heating in the presence of tert-butylisocyanide to form ketene imine, which is then refined to 56 through electrocyclic ring closure.



Scheme 1.11

II. CONCLUSION

As seen from the examples given in this chapter, Group 6 metallocarbene complexes are reactive towards a variety of nitrogen-containing substrates, resulting different of mono-/poly-heterocyclic products. Generally, 4 to 7 membered rings can be prepared in one step with high selection. Among these, simple nitrogen heterocycle formation appears to be both mechanically and synthetically of particular relevance.

In addition, further work is needed to fully characterize the electronic properties of transition metal carbene complexes in the synthesis of azaheterocycles. For example, (i) the development of a stepwise or one-pot process similar to those well known in terminal carbocycle synthesis would be welcome; (ii) new asymmetric methods or strategies should be developed to improve the performance of metal complexes in enantioselective heterocycle synthesis; (iii) Undoubtedly, the use of stoichiometric amounts of metal reagents can be considered a significant and common drawback of the carbene complex-based synthesis strategy. A new concept that requires special attention is the developement of catalytic processes that will benefit all the resources of these systems.

REFERENCE

[1] For the Nobel laureate lectures, see: (a) Chauvin, Y. Angew. Chem., Int. Ed. **2006**, 45, 3740. (b) Grubbs, R. H. Angew. Chem., Int. Ed. **2006**, 45, 3748. (c) Schröck, R. R. Angew. Chem., Int. Ed. **2006**, 45, 3760.

[2] (a) Fischer, E. O.; Maasböl, A. Angew. Chem., Int. Ed. **1964**, 3, 580. (b) Mills, O. S.; Redhouse, A. D. Angew. Chem., Int. Ed. **1965**, 4, 1082.

[3] Several reviews have appeared in the past 25 years. General reviews: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U. Transition Metal Carbene Complexes; Verlag Chemie: Weinheim, Germany, 1983. (b) Dötz, K. H. Angew. Chem., Int. Ed. **1984**, 23, 587. (c) Zaragoza Dörwald, F. Metal Carbenes in Organic Synthesis; Wiley VCH: Weinheim, Germany, 1999. (d) Herndon, J. W. Coord. Chem. Rev. **2000**, 206-207, 237. (e) Dötz, K. H.; Jahr, H. C. In Carbene Chemistry; Bertrand, G., Ed.; Fontis Media S. A.: Lausanne, Switzerland/ Marcel Dekker: New York, 2002; p 231. (f) Dötz, K. H.; Minatti, A. In Transition Metals for Organic Synthesis, 2nd ed.; Beller, M., Bolm, C., Eds.; Wiley- VCH: Weinheim, Germany, 2004; p 397. (g) Wu, Y.-T.; de Meijere, A. Top. Organomet. Chem. **2004**, 13, 21. (h) Wu, Y.-T.; Kurahashi, T.; de Meijere, A. J. Organomet. Chem. **2005**, 690, 5900. (i) Dötz, K. H.; Koch, A.; Werner, M. In Handbook of Functionalized Organometallics; Knochel, P., Ed.; Wiley-VCH: Weinheim, Germany, 2005; p 451. (j) Aumann, R. Adv. Organomet. Chem. **1997**, 41, 163. (k) Aumann, R. Eur. J. Org. Chem. **2000**, 17. (l) de Meijere, A.; Schirmer, H.; Duetsch, M. Angew. Chem., Int. Ed. **2000**, 39, 3964. Chemistry of carbohydrate metal carbene complexes: (m) Dötz, K. H.; Ehlenz, R. Chem. Eur. J. **1997**, 3, 1751. (n) Dötz, K. H.; Jäkel, C.; Haase, W.-C. J. Organomet. Chem. **2001**, 617-618, 119. Cycloaddition reactions of Fischer carbene complexes: (o) Wulff, W. D. In Comprehensive Organic Synthesis, Vol. 5; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; p 1065. (p) Wulff, W. D. In Comprehensive Organometallic Chemistry II; Abel, E. W., Stone, F. G. A., Wilkinson, Eds.; Pergamon Press: New York, 1995; p 469. (q) Lautens, M.; Klute, W.; Tam, W. Chem. Rev. **1996**, 96, 49. (r) Harvey, D. F.; Sigano, D. M. Chem. Rev. **1996**, 96, 271. (s) Frühauf, H.-W. Chem. Rev. **1997**, 97, 523. (t) Barluenga, J.; Rodríguez, F.; Fañanás, F. J.; Flórez, J. Top. Organomet. Chem. **2004**, 13, 59. Preparation of five-membered carbocyclic rings: (u) Herndon, J. W. Tetrahedron **2000**, 56, 1257. Carbene complexes in the synthesis of heterocycles: (v) Barluenga, J. Pure Appl. Chem. **2002**, 74, 1317. (w) Barluenga, J.; Santamaría, J.; Tomás, M. Chem. Rev. **2004**, 104, 2259. (x) Barluenga, J.; Martínez, S. Arkivoc **2006**, Vii, 129. (y) Kagoshima, H.; Fuchibe, K.; Akiyama, T. Chem. Rec. **2007**, 7, 104. Single electron transfer (SET) reactions of Fischer carbene complexes: (z) Sierra, M. A.; Gómez-Gallego, M.; Martínez-Álvarez, R. Chem. Eur. J. **2007**, 13, 736. Nitrogen-ylide carbene complexes in organic synthesis: (aa) Rudler, H.; Parlier, A. Trends Organomet. Chem. **1999**, 3, 113. Chemistry of cyclopropylcarbene metal complexes: (ab) Herndon, J. W. Curr. Org. Chem. **2003**, 7, 329. Carbene complexes in the synthesis of optically active molecules: (ac) Santamaría, J. Curr. Org. Chem. **2009**, 13, 31. Fischer carbene complexes in eneyne metathesis: (ad) Diver, S. T.; Giessert, A. J. Chem. Rev. **2004**, 104, 1317. Computational tools in the chemistry of metal carbene complexes: (ae) Frenking, G.; Solá, M.; Vyboishchikov, S. F. J. Organomet. Chem. **2005**, 690, 6178. (af) Sierra, M. A.; Fernández, I.; Cossío, F. P. Chem. Commun. **2008**, 4671. Physical organic chemistry of Fischer carbene complexes: (ag) Bernasconi, C. F. Adv. Phys. Org. Chem. **2002**, 37, 137. (ah) Bernasconi, C. F. Chem. Soc. Rev. **1997**, 26, 299.

[4] Fischer, E. O.; Maasböl, A. Chem. Ber. **1967**, 100, 2445.

[5] (a) Fischer, E. O.; Aumann, R. Angew. Chem., Int. Ed. **1967**, 6, 879. (b) Fischer, E. O.; Aumann, R. Chem. Ber. **1968**, 101, 954. (c) Casey, C. P.; Cyr, C. R.; Boggs, R. A. Synth. Inorg. Metal-Org. Chem. **1973**, 3, 249. (d) Harvey, D. F.; Brown, M. F. Tetrahedron Lett. **1990**, 31, 2529. (e) Xu, Y. C.; Wulff, W. D. J. Org. Chem. **1987**, 52, 3263.

[6] (a) Hoye, T. R.; Chen, K.; Vyvyan, J. R. Organometallics **1993**, 12, 2806. (b) Zheng, Q.-H.; Su, J. Synth. Commun. **2000**, 30, 177.

[7] This concept was first applied in the late 1960s/early 1970s: (a)Öfele, K. Angew. Chem., Int. Ed. **1968**, 7, 950. (b) Rees, C. W.; von Angerer, E. J. Chem. Soc., Chem. Commun. **1972**, 420.

[8] (a) Semmelhack, M. F.; Lee, S. R. Organometallics **1987**, 6, 1839. (b) Imwinkelried, R.; Hegedus, L. S. Organometallics **1988**, 7, 702. (c) Schwindt, M. A.; Lejon, T.; Hegedus, L. S. Organometallics **1990**, 9, 2814.

[9] (a) Fischer, E. O.; Röll, W.; Hoa Tran Huy, N.; Ackermann, K. Chem. Ber. **1982**, 115, 1951. (b) Hoa Tran Huy, N.; Lefloch, P.; Robert, F.; Jeannin, Y. J. Organomet. Chem. **1987**, 327, 211. (c) Neidlein, R.; Gürtler, S.; Krieger, C. Helv. Chim. Acta **1994**, 77, 2303. (d) Havránek, M.; Huák, M.; Dvořák, D. Organometallics **1995**, 14, 5024. (e) Dötz, K. H.; Tomuschat, P.; Nieger, M. Chem. Ber. **1997**, 130, 1605. (f) Crause, C.; Goerls, H.; Lotz, S. Dalton Trans. **2005**, 1649.

[10] (a) Reviews: Sierra, M. A. Chem. Rev. **2000**, 100, 3591. (b) Berger, A.; Djukic, J.-P.; Michon, C. Coord. Chem. Rev. **2002**, 225, 215.
[11] (a) Knochel, P.; Stadtmüller, H. Organometallics **1995**, 14, 3163. (b) Cooper, N. J.; Lee, I. J. Am. Chem. Soc. **1993**, 115, 4389.
[12] (a) Weyershausen, B.; Dötz, K. H. Eur. J. Inorg. Chem. **1999**, 1057. (b) McDonald, F. E. Chem. Eur. J. **1999**, 5, 3103. (c) Ulrich, K.; Porhiel, E.; Péron, V.; Ferrand, V.; Le Bozec, H. J. Organomet. Chem. **2000**, 601, 78. (d) McDonald, F. E.; Gleason, M. M. J. Am. Chem. Soc. **1996**, 118, 6648. (e) McDonald, F. E.; Reddy, K. S.; Díaz, Y. J. Am. Chem. Soc. **2000**, 122, 4304. (f) Alcázar, E.; Pletcher, J. M.; McDonald, F. E. Org. Lett. **2004**, 6, 3877. (g) Koo, B.; McDonald, F. E. Org. Lett. **2007**, 9, 1737.
[13] http://www2.chemistry.msu.edu/faculty/wulff/myweb26/research/carbenes.htm
[14] Pfeiffer, J.; Nieger, M.; Do¨tz, K. H. Eur. J. Org. Chem. **1998**, 1011.
[15] Fischer, E. O.; Kreis, G.; Kreiter, C. G.; Müller, J.; Huttner, G.; Lorenz, H. Angew. Chem., Int. Ed. **1973**, 12, 564.
[16] In some cases, metal carbyne complexes may serve as precursors for carbene complexes that otherwise are difficult to obtain: Kreissl, F. R. In Carbyne Complexes; Fischer, H., Hofmann, P., Kreissl, F. R., Schrock, R. R., Schubert, U., Weiss, K., Eds.; VCH: Weinheim, Germany, 1988; p 114.
[17] (a) Kreiter, C. G. Angew. Chem., Int. Ed. **1968**, 7, 390. (b) Casey, C. P.; Anderson, R. L. J. Am. Chem. Soc. **1974**, 96, 1230. (c) Bernasconi, C. F.; Sun, W. J. Am. Chem. Soc. **1993**, 115, 12526. (d) Bernasconi, C. F.; Sun, W. Organometallics **1997**, 16, 1926. (e) Bernasconi, C. F.; Sun, W.; García-Rio, L.; Yan, K.; Kittredge, K. J. Am. Chem. Soc. **1997**, 119, 5583.
[18] Barluenga, J.; Fañanás-Mastral, M.; Aznar, F. Chem. Eur. J. **2008**, 14, 7508.
[19] For recent treatises on this topic, see: Templates in Chemistry I and II: (a) Schalley, C. A.; Vögtle, F.; Dötz, K. H., Eds. Top. Curr. Chem. **2005**, 248. (b) Schalley, C. A.; Vögtle, F.; Dötz, K. H., Eds. Top. Curr. Chem. **2005**, 249.
[20] Review: Barluenga, J.; Flórez, J.; Fanñanás, F. J. J. Organomet. Chem. **2001**, 624, 5.
[21] Alcaide, B.; Casarrubios, L.; Domínguez, G.; Sierra, M. A. Curr. Org. Chem. **1998**, 2, 551.
[22] Kreissl, F. R.; Fischer, E. O.; Kreiter, C. G. J. Organomet. Chem. **1973**, 57, C9.
[23] Chan, K. S.; Wulff, W. D. J. Am. Chem. Soc. **1986**, 108, 5229.
[24] Baldoli, C.; del Buttero, P.; Licandro, E.; Maiorana, S.; Papagni, A.; Zanotti-Gerosa, A. J. Organomet. Chem. **1994**, 476, C27.
[25] Barluenga, J. Pure Appl. Chem. **2002**, 74, 1317.
[26] (a) Barluenga, J.; Fernández-Marí, F.; Viado, A. L.; Aguilar, E.; Olano, B. J. Chem. Soc., Perkin Trans. 1 **1997**, 2267. (b) Barluenga, J.; Fernández-Marí, F.; Viado, A. L.; Aguilar, E.; Olano, B.; García-Granda, S.; Moya-Rubiera, C. Chem. Eur. J. **1999**, 5, 883.
[27] (a) Barluenga, J.; Fernández-Marí, F.; Aguilar, E.; Viado, A. L.; Olano, B. Tetrahedron Lett. **1998**, 39, 4887. (b) Barluenga, J.; Fernández-Marí, F.; González, R.; Aguilar, E.; Revelli, G. A.; Viado, A. L.; Fañanás, F. J.; Olano, B. Eur. J. Org. Chem. **2000**, 1773.
[28] Barluenga, J.; Fernández-Rodríguez, M. A.; Aguilar, E.; Fernández- Marí, F.; Salinas, A.; Olano, B. Chem. Eur. J. **2001**, 7, 3533.
[29] (a) Barluenga, J.; Tomás, M.; López-Pelegrín, J. A.; Rubio, E. Tetrahedron Lett. **1997**, 38, 3981. (b) Aumann, R.; Yu, Z.; Fröhlich, R. J. Organomet. Chem. **1997**, 549, 311.
[30] Barluenga, J.; Tomás, M.; Ballesteros, A.; Santamaría, J.; Suárez-Sobrino, A. J. Org. Chem. **1997**, 62, 9229.
[31] Barluenga, J.; López, L. A.; Martínez, S.; Tomás, M. Synlett **1999**, 219.