DOI: 10.1002/chem.200701109

Diastereoselective Synthesis of Three-, Five-, Six-, and Seven-Membered Rings from Fischer Carbene Complexes and 4-Unsubstituted 1-Amino-1,3-Dienes

Fernando Aznar,* Martín Fañanás-Mastral, Jorge Alonso, and Francisco J. Fañanás*[a]

Abstract: Fischer carbene complexes react with 4-unsubstituted 1-amino-1,3-dienes to give different carbocyclization products depending on the nature of the carbene complex and on the substitution pattern of the aminodiene. Thus, the reaction of arylcarbene chromium complexes and 1-aminodienes diastereoselectively affords cyclopropane derivatives by means of a formal [2+1] carbocyclization reaction. In particular, pentacarbonyl[(2-furyl)-(methoxy)methylene]chromium complex furnishes formal [4+1] carbocyclization products. Starting from β-substituted alkenylcarbene complexes, formal [4+1] reactions occur and cyclopentenamine derivatives are diastereoselectively formed. However, when the α,β-disubstituted alkenylcarbene complex pentacarbonyl[(5,6-dihydro-2*H*-pyran-2-yl)(methoxy)methylene]-tungsten is used, the outcome of the reaction depends on the substitution on the carbon atom at the 3-position of the aminodiene, generating the [3+2] or [4+3]-cyclization products if the substituent is or is not a hydrogen atom, respectively. Finally, when the reaction is performed with alkynylcarbene complexes, benzaldehyde derivatives are obtained if the triple-bond substituent is a phenyl group or indene derivatives if the group is an alkenyl moiety.

Keywords: aminodienes · carbenes · cyclization · diastereoselectivity · organic synthesis

Introduction

The search for new methodologies for the selective synthesis of small- and medium-sized carbocycles continues to be of great interest for organic chemists[1] due to the presence of these skeletons in biologically relevant compounds.[2] Organometallic compounds have considerably contributed to the development of important processes for the construction of cyclic products with different ring sizes.[3] In this context, Fischer carbene complexes have proved to be very efficient and extraordinarily versatile starting materials for carrying out a wide range of cycloaddition reactions, which provide a great array of carbocyclic and heterocyclic ring systems with a high degree of selectivity in most cases.[4,5] In particular, the reaction of stabilized Group 6 carbene complexes and aminodienes has resulted to be an interesting entry for the preparation of five-, six-, and seven-membered carbo- and heterocycles. Thus, reactions of aryl and alkenylcarbene complexes with 1,3-diamino-1,3-dienes leads to the formation of formal [4+1] cyclopentenones.[6] Nevertheless, 1-amino-1-aza-1,3-dienes and chromium alkenylcarbene complexes also undergo cyclopentannulation to furnish [3+2]-substituted cyclopentenes in a regio and disatereoselective way along with minor amounts of [4+1] pyrrole derivatives.[7] While 2-amino-1,3-butadienes react with Group 6 arylcarbene complexes giving the metathesis products,[8] α,β-unsaturated boroxy-[9] and methoxycarbene[10] complexes lead to the corresponding [4+2] cycloaddition products. Interestingly, the use of β-substituted methoxy alkenyl chromium carbenes instead of the corresponding tungsten derivatives produces a substantial change on the reaction outcome and the formal [4+3] cycloheptadienone derivatives are obtained.[6,11] [4+3] Heterocyclizations have been successfully effected by starting from 4-amino-1-aza-1,3-dienes and unsaturated carbene complexes.[12] Imines derived from pyrrole- and indolecarbaldehydes, which can be considered as 3-amino-1-aza-1,3-diene derivatives, react with unsaturated carbene complexes giving rise to the formal [3+3] or [4+3][13] cycloadducts depending on the substitution pattern

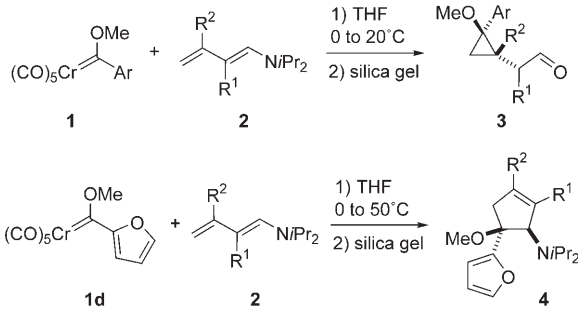
[a] Prof. Dr. F. Aznar, M. Fañanás-Mastral, Dr. J. Alonso, Prof. Dr. F. J. Fañanás
Instituto Universitario de Química Organometálica "Enrique Moles", Unidad Asociada al CSIC
Universidad de Oviedo, Julián Clavería 8
33006 Oviedo (Spain)
Fax: (+34) 985-103-450
E-mail: fag@uniovi.es
fjfv@uniovi.es

of the heterocyclic nitrogen. Finally, 2-amino-1,3-butadienes can also participate in reactions with alkynylcarbene complexes. Particularly when aryl- and alkenylalkynylcarbene complexes were used, mono, double, or triple [4+2] cycloaddition–cyclopentannulation tandem reactions were observed.[14] Considering that 1-aminodienes have been scarcely used in these types of transformations, we present herein the reaction of Group 6 carbene complexes and 4-unsubstituted 1-amino-1,3-butadienes to afford three-, five-, six-, and seven-membered carbocyclic rings in a diastereoselective way. Formal [2+1], [3+2], [4+2], and [4+3] cyclization reactions are observed and the reaction outcome depends on the nature of the substituents of both the 1-aminodiene and the carbene complex, and also on the metal of the carbene complex.

Results and Discussion

Taking into account that the results of the reaction of carbene complexes and 4-unsubstituted 1-aminodienes are highly dependent on the nature of the substituent of the carbene complex used, the results and discussion have been systematized according to the structure of these starting complexes.

Aryl carbene complexes. Formal [2+1] cyclizations: When arylcarbene chromium complexes **1** were treated with one equivalent of 1-aminodienes **2** in THF at temperatures ranging between 0 and 20°C, cyclopropane derivatives **3** were obtained, after hydrolysis with silica gel, in moderate yield and as single diastereoisomers (Scheme 1 and Table 1).



Scheme 1. Reaction of arylcarbene complexes **1** and 4-unsubstituted 1,3-aminodienes **2** to give cyclopropane derivatives **3** and cyclopentenamines **4**.

Compounds **3** can be considered as a result of a formal [2+1] carbocyclization reaction, in which the aminodiene acts as synthon of two carbon units and the carbene complex as a synthon of one carbon unit. The structure and relative configuration of the stereogenic centers of compounds **3a**–**e** were determined by 2D NMR spectroscopic analysis (COSY, HMQC, HMBC, and NOESY).

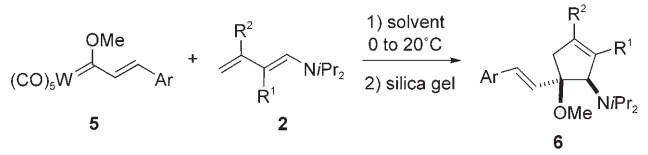
It is interesting to note that the reaction of furylcarbene complex **1d** with aminodienes **2** under the same reaction conditions does not proceed and it is necessary to warm to 50°C for complete consumption of the starting carbene complex. Under these new reaction conditions, the formal [4+1] cyclopentenamine derivatives **4**, in which the aminodiene has acted as a four-unit component and the carbene complex as a one-unit component, are isolated (Scheme 1 and Table 1). Also remarkable is that all these reactions did not proceed when using the corresponding tungsten carbene complexes.

Table 1. Cyclopropane derivatives **3** and cyclopentenamines **4** from arylcarbene complexes **1** and 1-aminodienes **2**.

Carbene complex	Ar	Aminodiene	R^1	R^2	Product	Yield [%][a]
1a	Ph	**2a**	H	H	**3a**	62
1a	Ph	**2b**	H	Me	**3b**	70
1a	Ph	**2c**	Me	H	**3c**	73
1b	1-Naph[b]	**2a**	H	H	**3d**	52
1c	2-Fu[c]	**2b**	H	Me	**4a**	62
1c	2-Fu[c]	**2c**	Me	H	**4b**	60

[a] Isolated yield based on starting carbene complexes **1**. [b] 1-Naphthyl. [c] 2-Furyl.

Alkenylcarbene complexes. Formal [4+1], [3+2], and [4+3] cyclization reactions: Next, we decided to investigate the behavior of alkenylcarbene complexes towards aminodienes **2**. Initially, we began the study with β-substituted alkenylcarbene complexes **5**. Therefore, reaction of aminodienes **2** with alkenylcarbene tungsten complexes **5** in diethyl ether or THF at temperatures ranging between 0 and 20°C gave rise, after hydrolysis with silica gel, to cyclopentenamine derivatives **6** in good yields and with high diastereoselectivity (Scheme 2 and Table 2). This transformation can be consid-



Scheme 2. Reaction of β-substituted alkenylcarbene complexes **5** and aminodienes **2** to give cyclopentenamine derivatives **6**.

Table 2. Cyclopentenamine derivatives **6** from alkenylcarbene complexes **5** and aminodienes **2**.

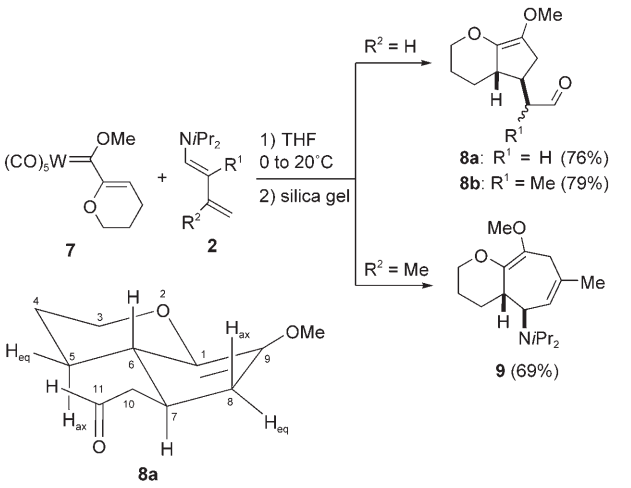
Entry	Carbene complex	Ar	Amino diene	R^1	R^2	Solvent	Product	Yield [%][a] (*de* [%])[b]
1	**5a**	Ph	**2a**	H	H	Et_2O	**6a**	78 (65)
2	**5a**	Ph	**2a**	H	H	THF	**6a**	81 (87)
3	**5a**	Ph	**2b**	H	Me	Et_2O	**6b**	81 (68)
4	**5a**	Ph	**2b**	H	Me	THF	**6b**	89 (90)
5	**5b**	Fu[c]	**2b**	H	Me	Et_2O	**6c**	86 (60)[d]
6	**5b**	Fu[c]	**2b**	H	Me	THF	**6c**	80 (80)[d]
7	**5a**	Ph	**2c**	Me	H	THF	**6d**	73 (>95)
8	**5b**	Fu[c]	**2c**	Me	H	THF	**6e**	71 (80)

[a] Isolated yield based on starting carbene complexes **5**. [b] The diastereoisomeric excess was determined by ^{1}H NMR spectroscopy on the reaction crude. [c] 2-Furyl. [d] Compound **6c** and diast-**6c** can be separated by column chromatography.

ered as a formal [4+1] cyclization reaction. The structure and configuration of the stereogenic centers formed were determined by 2D NMR spectroscopic analysis (COSY, HMQC, HMBC, and NOESY) carried out on **6d**.

From the results summarized in Table 2, it can be inferred that a more polar solvent, THF versus Et_2O, increases the diastereoselectivity of the reaction (Table 2, entries 1–6). The presence of a heteroatom in the aryl substituent of the carbene complex produces a slight decrease in the diastereoselectivity (Table 2, entries 4, 6, 7, and 8). The substitution pattern of the aminodiene also influences on the diastereoselectivity. So, substitution at the 3-position of the aminodiene leads to better diastereoselectivities (Table 2, entry 7).

A different reaction outcome was observed when α,β-disubstituted alkenyl–tungsten carbene complex **7** was used.[15] Thus, treatment of carbene complex **7** with aminodienes **2a**,**b** under the same reaction conditions as above described led, after hydrolysis, to cyclopenta[*b*]pyrane derivatives **8** in good yields (Scheme 3). These compounds could be considered as a formal [4+1] cyclization reaction. The structure and configuration of the stereogenic centers formed were determined by 2D NMR spectroscopic analysis (COSY, HMQC, HMBC, and NOESY) carried out on **6d**.



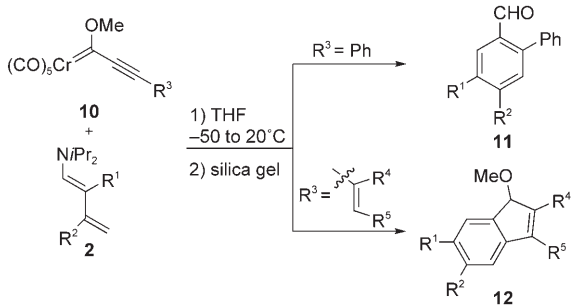
Scheme 3. Reaction of α,β-substituted alkenylcarbene complex **7** and aminodienes **2** to give cyclopenta[*b*]pyrane and cyclohepta[*b*]pyranamine derivatives **8** and **9**.

From the results summarized in Table 2, it can be inferred that a more polar solvent, THF versus Et_2O, increases the diastereoselectivity of the reaction (Table 2, entries 1–6). The presence of a heteroatom in the aryl substituent of the carbene complex produces a slight decrease in the diastereoselectivity (Table 2, entries 4, 6, 7, and 8). The substitution pattern of the aminodiene also influences on the diastereoselectivity. So, substitution at the 3-position of the aminodiene leads to better diastereoselectivities (Table 2, entry 7).

A different reaction outcome was observed when α,β-disubstituted alkenyl–tungsten carbene complex **7** was used.[15] Thus, treatment of carbene complex **7** with aminodienes **2a**,**b** under the same reaction conditions as above described led, after hydrolysis, to cyclopenta[*b*]pyrane derivatives **8** in good yields (Scheme 3). These compounds could be considered formal [3+2] cyclization products, in which the carbene complex has acted as a synthon of three carbon units and the aminodiene as a synthon of two carbon units. Although compound **8b** was obtained as a mixture of two diastereoisomers, it is interesting to remark that the cyclization reaction is a completely diastereoselective process and the observed diastereoselectivity comes from the formation of two epimers at the α-position of the aldehyde. Attempts to equilibrate this mixture to give a single diastereoisomer by treatment with catalytic amounts of acid or base were unsuccessful.

The structure of compounds **8** was unequivocally determined by 2D NMR experiments (COSY, HMQC, and HMBC) carried out on compound **8a**. The same chemical shift for H6 and H7 protons did not allow us to clearly determine the relative configuration of the stereogenic centers of the ring system and it was ascertained by the coupling constants and selective NOE experiments. The quartet of doublets signal for $H5_{ax}$ ($\delta = 0.92$ ppm, $J = 12.9$, 3.6 Hz) fixes an axial disposition for the H6 proton. The cross peaks on the resolved *J* 2D spectrum allow the assignation of H8 protons and fix an axial disposition for the H7 proton as a consequence of the triplet signal for $H8_{ax}$ ($\delta = 1.93$ ppm, $J = 12.1$ Hz). Moreover, the selective NOE experiments place H11 and $H5_{eq}$ protons on the same face of the molecule and confirm the axial disposition of H6 and H7 protons. Conversely, when the carbene complex **7** was reacted with the 3-substituted aminodiene **2c** under the same reaction conditions, a different reaction outcome was observed and the formal [4+3] cyclization cyclohepta[*b*]pyranamine derivative **9** (four carbon units come from the aminodiene and three from the carbene complex) was formed in 69% yield as a unique diastereoisomer, as deduced from the 2D NMR spectroscopic analysis (Scheme 3).

Alkynylcarbene complexes. Formal [4+2] cyclization and cascade reactions: Considering the influence of the nature of the group bound to the carbene carbon of the carbene complex, we decided to further study the behavior of alkynylcarbene complexes in this chemistry. Initially, arylalkynylcarbene complex **10a** was treated with aminodienes **2** in THF at temperatures ranging between −50 and 0 °C leading, after hydrolysis, to the corresponding benzaldehyde derivatives **11** in good yields. However, a different result was achieved when starting from alkenylalkynylcarbene complexes **10b**,**c** which reacted with aminodienes **2** under the same reaction conditions to afford indene derivatives **12** in moderate to good yields (Scheme 4 and Table 3).



Scheme 4. Reaction of carbene complexes **10** and aminodienes **2** to give benzaldehydes **11** and indene derivatives **12**.

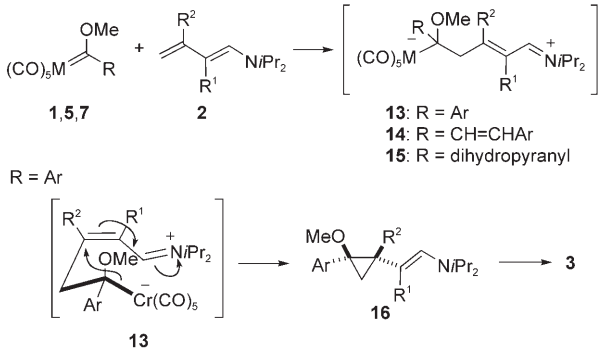
Mechanistic proposals: Tentative mechanisms to rationalize the formation of the different products obtained in the reaction of carbene complexes **1**, **5**, **7**, and **10** and aminodienes **2** are presented. We assume in the first place that a 1,2-addition of the distal carbon atom of the aminodiene **2** to the carbene complexes **1**, **5**, and **7** occurs to form intermediates **13**, **14**, or **15**. The evolution of these intermediates depends on the nature of the R group of the carbene complex. Thus, when R is an aryl group, a Michael addition of the carbon

Table 3. Benzaldehydes **11** and indene derivatives **12** from alkynylcarbene complexes **10** and 1-aminodienes **2**.

Carbene complex	R^3	Aminodiene	R^1	R^2	Product	Yield [%][a]
10a	Ph	**2a**	H	H	**11a**	66
10a	Ph	**2b**	H	Me	**11b**	70
10a	Ph	**2c**	Me	H	**11c**	72
10b	R^4-R^5=$(CH_2)_4$	**2b**	H	Me	**12a**	61
10c	R^4=H, R^5=Ph	**2a**	H	H	**12b**	55

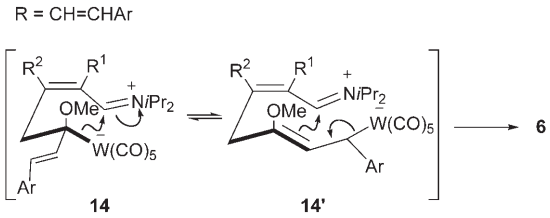
[a] Isolated yield based on starting carbene complexes **10**.

atom attached to the pentacarbonylmetalate to the unsaturated immonium moiety in intermediates **13** would lead to the cyclic systems **16**, which after hydrolysis, would give rise to the cyclopropane derivatives **3**. Formation of products **4** could be accounted for considering a nucleophilic attack of the carbon atom of the allylpentacarbonylmetallate to the immonium group in intermediates **13**. Moreover, the complete diastereoselectivity found in the formation of compounds **3** could be attributed to transition states with the same geometric disposition as intermediates **13**, probably favored by an electrostatic interaction between the negatively charged pentacarbonylmetal fragment and the positively charged immonium group. Consequently, the smaller methoxy group would be positioned on the side of the R^1 and R^2 groups (Scheme 5).



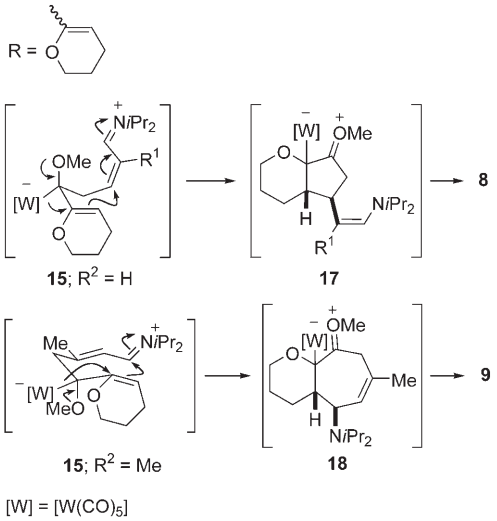
Scheme 5. Mechanistic proposal for the formation of cyclopropane derivatives **3**.

The evolution of intermediates **14**, bearing an alkenyl group, depends on the substitution pattern of the double bond. Thus for β-substituted alkenyl groups, we could consider that intermediate **14** could be in equilibrium with **14′**, derived from an 1,3-migration[16] of the pentacarbonylmetal. A nucleophilic attack of the γ-carbon atom of the allylpentacarbonylmetallate to the carbon atom of the immonium moiety in intermediates **14′** would lead to the cyclopentenamines **6**, after hydrolysis and metal decoordination. Alternatively, compounds **6** could be formed by an attack of the α-carbon atom of the allylmetallate moiety of intermediate **14** to the immonium group (Scheme 6). The high diastereoselectivity found in the formation of compounds **6** could be attributed to transition states with the same geometric disposition as those shown in intermediates **14** and **14′**, respectively. Thus, the immonium and alkenyl moieties would be placed in a pseudoequatorial disposition on a chairlike transition state. A similar mechanism could account for the formation of compounds **4**.



Scheme 6. Mechanistic proposal for the formation of cyclopentenamine derivatives **6**.

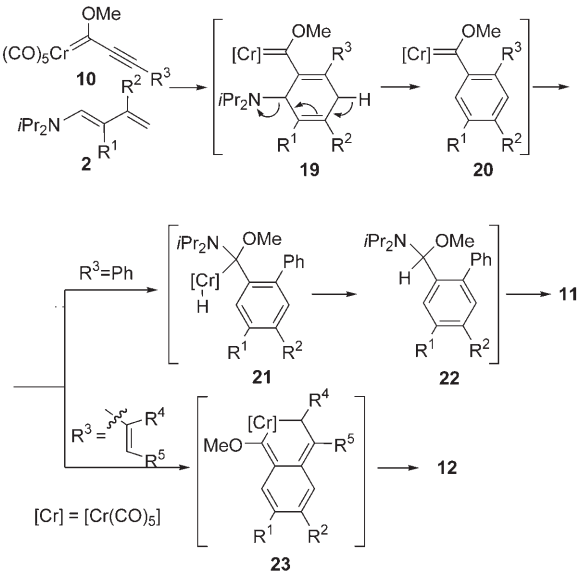
On the other hand, α,β-disubstituted alkenylcarbene complexes follow a different reaction pattern.[15] Moreover, the evolution of intermediates **15** is also different depending on the nature of the R^2 group. Thus, when the R^2 group is a hydrogen atom, intermediate **15** could undergo an intramolecular Michael addition of the allyltungstate to the unsaturated immonium moiety, presumably induced by a 1,2-migration[17] of the pentacarbonyltungsten fragment, affording the five-membered intermediate **17**. Further elimination of the metal moiety would furnish, after hydrolysis and metal decoordination, the cyclopentapyrane derivatives **8**. On the contrary, when the R^2 group is a methyl group, the Michael addition would as a result be disfavored by steric hindrance of the methyl group. In these circumstances, a nucleophilic attack to the immonium carbon atom would be preferred and the seven-membered intermediate **18** would be formed. Elimination of the metal fragment would furnish the cycloheptapyrane derivative **9** (Scheme 7).



Scheme 7. Mechanistic proposal for the formation of cyclopentapyrane and cycloheptapyrane derivatives **8** and **9**.

The complete diastereoselectivity found in the formation of compounds **8** and **9** could be attributed to transition states with the same geometric disposition as intermediates **15** ($R^2=H$ or $R^2=Me$), in which the unsaturated immonium or the immonium moiety, respectively, would be placed in a pseudoequatorial disposition on the chairlike transition state, thus avoiding the interaction with the sterically demanding methylene group of the dihydropyranyl moiety.

Finally, in Scheme 8, a tentative proposal to account for the formation of products **11** and **12** is presented. We first consider a formal [4+2] cycloaddition reaction, probably by



Scheme 8. Mechanistic proposal for the formation of benzaldehyde and indene derivatives **11** and **12**.

a successive Michael addition of the distal carbon atom of the 1-aminodiene **2** to the alkynylcarbene complex **10** and further cyclization, giving intermediate **19**. Subsequent elimination of diisopropylamine would lead to arylcarbene complexes **20**. The evolution of these intermediates depends on the nature of the R^3 substituent. In the case that R^3 is a phenyl group, the diisopropylamine generated in the aromatization process could be added to the carbene carbon atom of **20**, giving the intermediate **21**, which could undergo a reductive elimination to afford the addition product **22**. Final acid hydrolysis would furnish the benzaldehyde derivatives **11**. Conversely, when R^3 is an alkenyl group, arylcarbene complexes **20** could evolve through an electrocyclic reaction leading to cromacyclohexadiene derivatives **23**. Subsequent reductive elimination would afford indene derivatives **12**. The different behavior of intermediate **20** could be attributed to the increase in activation energy required for the cyclopentannulation in a system containing two aromatic rings.

Conclusion

We have described the reaction of Group 6 carbene complexes and 1-amino-1,3-butadienes. The reaction outcome highly depends on the structure of the carbene complex. Thus, starting from arylcarbene chromium complexes, cyclopropane derivatives derived from a formal [2+1] carbocyclization reaction are diastereoselectively obtained. Only for the furylcarbene complex, a formal [4+1] carbocyclization reaction was observed. In the case of β-substituted alkenylcarbene complexes, formation of five-membered rings by formal [4+1] carbocyclization reactions occurs. Conversely, α,β-disubstituted alkenylcarbene complexes lead under the same reaction conditions to five- and seven-membered carbocycles by formal [3+2] and [4+3] carbocyclization reactions, with the substitution pattern on the 1-aminodiene responsible for the formation of the five- or seven-membered ring. On the other hand, reaction of alkynylcarbene chromium complexes with 1-aminodienes generates benzaldehyde or indene derivatives, with the substituent bound to the alkynyl moiety, phenyl, or alkenyl groups responsible for the formation of one or other product. Moreover, mechanistical proposals for all cyclization patterns have been discussed. Finally, it is important to point out the simplicity of the starting materials, 1-aminodienes, and Fischer-type carbene complexes.

Experimental Section

General: All reactions involving organometallic species were carried out under an atmosphere of dry N_2 by using oven-dried glassware and syringes. THF and Et_2O were distilled from sodium benzophenone ketyl under N_2 immediately prior to use. TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator (Scharlab). Flash column chromatography was carried out on commercial and deactivated silica gel 60, 230–240 mesh (deactivated silica gel was prepared as follows: silica gel (125 g) was stirred with a 4% aqueous solution of K_2HPO_4 (500 mL) for 3 h; after filtration, the resulting solid was oven-dried at 100 °C for 2 d). ^1H NMR (200, 300 MHz) and ^{13}C NMR (50.5, 75.5 MHz) spectra were measured at room temperature on Bruker AC-200, AV-300, and DPX-300 instruments, with tetramethylsilane (TMS) ($\delta=0.0$ ppm, ^1H NMR spectra) and $CDCl_3$ ($\delta=77.0$ ppm, ^{13}C NMR spectra), or C_6D_6 ($\delta=127.8$, ^{13}C NMR) as internal standards. Carbon multiplicities were assigned by DEPT techniques. Bidimensional NMR experiments (COSY, HMQC, HMBC, and NOESY) were recorded on a Bruker AMX-400 (400 MHz) and AV-600 (600 MHz). High-resolution mass spectra (HRMS) were determined on a Finnigang MAT95 spectrometer.

Materials: Carbene complexes **1a**,**b**,[18] **1c**,[19] **5**,[20] **7**,[21] **10a**,[22] and **10b**,**c**[23] were prepared according to literature procedures. 1-Amino-1,3-dienes were prepared according to the following procedure: The corresponding aldehyde (crotonaldehyde, 3-methyl-2-butenal, or *trans*-2-methyl-2-butenal; 10 mmol) was added to a solution of LDA, prepared from diisopropylamine (12.5 mmol) and BuLi (12.5 mmol, 1.6 M hexane solution) in THF (10 mL) at 0 °C under an argon atmosphere and the mixture was stirred 5 min. Chlorotrimethylsilane (15 mmol) was added to the resulting solution at the same temperature. The mixture was stirred for 30 min until the temperature reached room temperature. Solvents were removed and pentane (15 mL) was added to the resulting residue. The mixture was filtered and the pentane was removed from the filtrate to give the 1-amino-1,3-dienes **2**, which were used without further purification.

(*E*)-*N*,*N*-Diisopropyl-1,3-butadien-1-amine (2a): ^1H NMR (300 MHz, C_6D_6): $\delta=6.61$ (dt, $J=16.7$, 10.3 Hz, 1H; C*H*CH_2), 6.35 (d, $J=13.3$ Hz, 1H; =CHN), 5.37 (dd, $J=13.3$, 10.5 Hz, 1H; NCH=C*H*), 5.11 (d, $J=16.7$ Hz, 1H; CH*H*), 4.89 (dd, $J=10.5$ Hz, 1H; C*H*H), 3.27 (heptet, $J=$

6.7 Hz, 2H; 2×CHN), 0.91 ppm (d, J=6.7 Hz, 12H; 4×Me); ^{13}C NMR (DEPT, 75.5 MHz, C_6D_6): δ=138.5 (CH), 136.3 (CH), 103.1 (CH_2), 99.2 (CH), 45.7 (CH), 21.3 ppm (CH_3).

(*E*)-*N*,*N*-Diisopropyl-3-methyl-1,3-butadien-1-amine (2b): ^{1}H NMR (300 MHz, C_6D_6): δ=6.44 (d, J=14.1 Hz, 1H; =CHN), 5.49 (d, J=14.1 Hz, 1H; NCH=C*H*), 4.97 (brs, 1H; CH*H*), 4.80 (brs, 1H; C*H*H), 3.38 (heptet, J=6.7 Hz, 2H; 2×CHN), 2.03 (s, 3H; MeC=), 0.91 ppm (d, J=6.7 Hz, 12H; 4×*Me*CH); ^{13}C NMR (DEPT, 75.5 MHz, C_6D_6): δ=142.7 (C), 132.2 (CH), 104.9 (CH_2), 100.7 (CH), 45.8 (CH), 21.3 (CH_3), 19.6 ppm (CH_3).

(*E*)-*N*,*N*-Diisopropyl-2-methyl-1,3-butadien-1-amine (2c): ^{1}H NMR (300 MHz, C_6D_6): δ=6.59 (dd, J=16.5, 10.6 Hz, 1H; C*H*CH$_2$), 6.08 (s, 1H; =CHN), 5.05 (d, J=16.5 Hz, 1H; CH*H*), 4.90 (d, J=10.6 Hz, 1H; C*H*H), 3.24 (heptet, J=6.8 Hz, 2H; 2×CHN), 1.90 (s, 3H; MeC=), 0.91 ppm (d, J=6.8 Hz, 12H; 4×*Me*CH); ^{13}C NMR (DEPT, 75.5 MHz, C_6D_6): δ=141.9 (CH), 136.1 (CH), 115.6 (C),104.9 (CH_2), 48.4 (CH), 21.7 (CH_3), 12.7 ppm (CH_3).

General procedure for the preparation of compounds 3, 4, 6, 8, 9, 11, and 12: Carbene complexes **1**, **5**, **7**, or **10** (0.4 mmol) were added to a solution of the corresponding 1-amino-1,3-diene **2** (0.5 mmol) in THF (or diethyl ether) (10 mL) under an argon atmosphere at 0°C (50°C for alkynylcarbene complexes **10**). The mixture was stirred for 30 min until the temperature reached room temperature. The reaction mixture was quenched with a small amount of silica gel, solvents were removed and the resulting residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate 40:1 to 10:1) to give compounds **3**, **4**, **6**, **8**, **9**, **11**, and **12**.

2-[(1*R,2*S**)-2-Methoxy-2-phenylcyclopropyl]acetaldehyde (3a)**: Aminodiene **2a** (77 mg, 0.5 mmol) and carbene complex **1a** (125 mg, 0.4 mmol) afforded **3a** (47 mg, 62%) as a colorless oil. R_f: 0.46 (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=9.67 (t, J=1.6 Hz, 1H; CH=O), 7.41–7.32 (m, 5H; ArH), 3.18 (s, 3H; OMe), 2.17 (ddd, J=17.8, 7.2, 1.6 Hz, 1H; C*H*HCHO), 2.02, (ddd, J=17.8, 7.2, 1.6 Hz, 1H; CH*H*CHO), 1.79 (dtd, J=10.1, 7.2, 6.1 Hz, 1H; C*H*COMe), 1.30 (dd, J=10.1, 6.1 Hz, 1H; C*H*HCOMe), 1.00 ppm (t, J=6.1 Hz, 1H; CH*H*COMe); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ=201.2 (CH), 136.2 (C), 128.9 (CH), 128.3 (CH), 127.9 (CH), 79.8 (C), 54.3 (CH_3), 43.9 (CH_2), 20.0 (CH), 14.9 ppm (CH_2); HRMS (70 eV, EI): m/z: calcd for $C_{11}H_{13}O$: 161.0960 [M^+−CHO]; found: 161.0958.

2-[(1*R,2*S**)-2-Methoxy-1-methyl-2-phenylcyclopropyl]acetaldehyde (3b)**: Aminodiene **2b** (84 mg, 0.5 mmol) and carbene complex **1a** (125 mg, 0.4 mmol) afforded **3b** (57 mg, 70%) as a colorless oil. R_f: 0.49 (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=9.61 (t, J=2.2 Hz, 1H; CH=O), 7.42–7.32 (m, 5H; ArH), 3.18 (s, 3H; OMe), 2.13 (dd, J=16.8, 2.2 Hz, 1H; C*H*HCHO), 1.92 (dd, J=16.8, 2.2 Hz, 1H; CH*H*CHO), 1.45 (s, 3H; MeC), 1.26 (d, J=6.1 Hz, 1H; C*H*HCOMe), 0.90 ppm (d, J=6.1 Hz, 1H; CH*H*COMe); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ=202.1 (CH), 137.5 (C), 128.8 (CH), 128.3 (CH), 127.7 (CH), 70.0 (C), 54.7 (CH_3), 49.6 (CH_2), 28.1 (C), 20.1 (CH_2), 14.9 ppm (CH_3); HRMS (70 eV, EI): m/z: calcd for $C_{12}H_{15}O$: 175.1117 [M^+−CHO]; found: 175.1115.

2-[(1*R,2*S**)-2-Methoxy-2-phenylcyclopropyl]propanal (3c)**: Aminodiene **2c** (84 mg, 0.5 mmol) and carbene complex **1a** (125 mg, 0.4 mmol) afforded **3c** (60 mg, 73%, de) as a colorless oil. R_f: 0.51 (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=9.68 (s, 1H; CH=O), 7.48–7.32 (m, 5H; ArH), 3.18 (s, 3H; OMe), 1.42 (m, 1H; C*H*Me), 1.29 (m, 1H; C*H*COMe), 1.05 (t, J=6.8 Hz, 1H; C*H*HCOMe), 0.96 (d, J=6.7 Hz, 1H; *Me*CH), 0.92 ppm (dd, J=13.7, 6.8 Hz, 1H; CH*H*COMe); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ=203.8 (CH), 136.1 (C), 128.8 (CH), 128.3 (CH), 127.8 (CH), 67.3 (C), 54.4 (CH_3), 46.3 (CH_2), 28.0 (CH), 13.7 (CH_2), 13.0 ppm (CH_3).

2-[(1*R,2*S**)-2-Methoxy-2-(2-naphthyl)cyclopropyl]acetaldehyde (3d)**: Aminodiene **2a** (77 mg, 0.5 mmol) and carbene complex **1b** (145 mg, 0.4 mmol) afforded **3d** (50 mg, 52%) as a colorless oil. R_f: 0.42 (hexane/ethyl acetate 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ=9.64 (t, J=1.5 Hz, 1H; CH=O), 7.96–7.67 (m, 4H; ArH), 7.61–7.40 (m, 3H; ArH), 3.19 (s, 3H; OMe), 2.20 (ddd, J=12.5, 7.0, 1.5 Hz, 1H; C*H*HCHO), 2.11 (ddd, J=12.5, 7.0, 1.5 Hz, 1H; CH*H*CHO), 1.83 (dtd, J=10.2, 7.0, 6.6 Hz, 1H; C*H*COMe), 1.34 (dd, J=10.2, 5.9 Hz, 1H; C*H*HCOMe), 1.12 ppm (t, J=6.3 Hz, 1H; CH*H*COMe); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ=201.1 (CH), 137.8 (C), 133.9 (C), 133.0 (C), 128.3 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 126.8 (CH), 126.1 (CH), 125.1 (CH), 67.6 (C), 54.4 (CH_3), 43.8 (CH_2), 20.1 (CH), 14.7 ppm (CH_2).

(1*R,5*R**)-5-(2-Furyl)-*N*,*N*-diisopropyl-5-methoxy-3-methyl-2-cyclopentenamine (4a)**: Aminodiene **2b** (84 mg, 0.5 mmol) and carbene complex **1c** (121 mg, 0.4 mmol) afforded **4a** (69 mg, 62%) as a colorless oil. R_f: 0.57 (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.43 (d, J=1.8 Hz, 1H; =CHO), 6.32 (dd, J=3.1, 1.8 Hz, 1H; C*H*=CHO), 6.28 (d, J=3.1 Hz, 1H; C*H*CH=CHO), 5.43 (brs, 1H; =CH), 4.05 (brs, 1H; =CHC*H*N), 3.14–2.91 (m, 2H; 2×NC*H*Me), 3.05 (s, 3H; OMe), 2.83 (d, J=17.3 Hz, 1H; C*H*H), 2.57 (d, J=17.3 Hz, 1H; CH*H*), 1.84 (s, 3H; MeC=), 0.93 (d, J=6.0 Hz, 6H; 2×NCH*Me*Me), 0.85–0.60 ppm (m, 6H; 2×NCHMe*Me*); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ=154.4 (C), 141.7 (CH), 137.1 (C), 128.0 (CH), 109.5 (CH), 109.4 (CH), 88.4 (C), 72.2 (CH), 51.3 (CH_3), 45.6 (br; CH), 41.6 (CH_2), 23.1 (br; CH_3), 22.1 (CH_3), 17.0 ppm (CH_3); HRMS (70 eV, EI): m/z: calcd for $C_{17}H_{27}NO_2$: 277.2036 [M^+]; found: 277.2038.

(1*R,5*R**)-5-(2-Furyl)-*N*,*N*-diisopropyl-5-methoxy-2-methyl-2-cyclopentenamine (4b)**: Aminodiene **2c** (84 mg, 0.5 mmol) and carbene complex **1c** (121 mg, 0.4 mmol) afforded **4b** (67 mg, 60%) as a colorless oil. R_f: 0.60 (hexane/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.39 (brs, 1H; =CHO), 6.30 (d, J=3.1 Hz, 1H; C*H*=CHO), 6.18 (d, J=3.1 Hz, 1H; C*H*CH=CHO), 5.47 (brs, 1H; =CH), 3.79 (brs, 1H; =CHC*H*N), 3.32–3.19 (m, 1H; NC*H*Me), 3.07 (s, 3H; OMe), 3.03–2.82 (m, 1H; NC*H*Me), 2.76 (d, J=16.0 Hz, 1H; C*H*H), 2.50 (d, J=16.0 Hz, 1H; CH*H*), 1.66 (s, 3H; MeC=), 1.16 (d, J=6.6 Hz, 6H; 2×NCH*Me*Me), 1.03–0.95 ppm (m, 6H; 2×NCHMe*Me*); ^{13}C NMR (DEPT, 100 MHz, $CDCl_3$): δ=159.2 (C), 141.7 (CH), 140.5 (C), 123.0 (CH), 109.6 (CH), 106.6 (CH), 82.4 (C), 70.3 (CH), 51.8 (CH_3), 46.8 (br, CH), 43.6 (br; CH), 39.5 (CH_2), 23.4 (br; CH_3), 22.7 (br; CH_3), 15.8 ppm (CH_3); HRMS (70 eV, EI): m/z: calcd for $C_{17}H_{27}NO_2$: 277.2036 [M^+]; found: 277.2029.

(1*R,5*R**)-*N*,*N*-Diisopropyl-5-methoxy-5-[(*E*)-styryl]-2-cyclopentenamine (6a)**: Aminodiene **2a** (77 mg, 0.5 mmol) and carbene complex **5a** (188 mg, 0.4 mmol) afforded **6b** (93 mg, 78%, 65% *de* (*de*=diastereomeric excess) in Et_2O; 97 mg, 81%, 87% *de* in THF) as a colorless oil. R_f: 0.34 (hexane/ethyl acetate 5:1). ^{1}H NMR (300 MHz, C_6D_6): δ=7.29–7.02 (m, 5H; ArH), 6.48 (d, J=16.3 Hz, 1H; CH=C*H*Ar), 6.35 (d, J=16.3 Hz, 1H; C*H*=CHAr), 5.68 (ddt, J=6.0, 3.9, 2.0 Hz, 1H; =C*H*CHN), 5.62 (dq, J=6.0, 2.0 Hz, 1H; =C*H*CH$_2$), 3.78 (ddd, J=3.9, 2.0, 1.0 Hz, 1H; NCHC=), 3.15 (heptet, J=6.6 Hz, 1H; NC*H*Me), 3.13 (s, 3H; OMe), 2.52 (dq, J=16.7, 2.0 Hz, 1H; CH*H*), 2.27 (dtd, J=16.7, 2.2, 1.0 Hz, 1H; C*H*H), 1.15 (d, J=6.6 Hz, 1H; 2×*Me*CH), 0.96 ppm (d, J=6.6 Hz, 1H; 2×*Me*CH); ^{13}C NMR (DEPT, 75.5 MHz, C_6D_6): δ=137.6 (C), 134.9 (CH), 134.0 (CH), 128.6 (CH), 128.4 (CH), 127.6 (CH), 127.1 (CH), 126.4 (CH), 85.6 (C), 69.0 (CH), 51.5 (CH_3), 46.1 (CH), 39.3 (CH_2), 23.6 (CH_3), 22.6 ppm (CH_3); HRMS (70 eV, EI): m/z: calcd for $C_{20}H_{29}NO$: 299.2244 [M^+]; found: 299.2243.

(1*R,5*R**)-*N*,*N*-Diisopropyl-5-methoxy-3-methyl-5-[(*E*)-styryl]-2-cyclopentenamine (6b)**: Aminodiene **2b** (84 mg, 0.5 mmol) and carbene complex **5a** (188 mg, 0.4 mmol) afforded **6a** (102 mg, 81%, 68% *de* in Et_2O; 112 mg, 89%, 90% *de* in THF) as a colorless oil. R_f: 0.45 (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, C_6D_6): δ=7.34–7.02 (m, 5H; ArH), 6.52 (d, J=16.4 Hz, 1H; PhC*H*=CH), 6.39 (d, J=16.4 Hz, 1H; PhCH=C*H*), 5.32 (brs, 1H; MeC=C*H*), 3.82 (brs, 1H; CHN), 3.28–3.12 (m, 2H; 2×NC*H*Me), 3.18 (s, 3H; OMe), 2.51 (d, J=16.4 Hz, 1H; C*H*H), 2.16 (d, J=16.4 Hz, 1H; CH*H*), 1.64 (s, 3H; MeC=), 1.18 (d, J=6.7 Hz, 6H; 2×NCH*Me*Me), 1.02 ppm (d, J=6.7 Hz, 6H; 2×NCHMe*Me*); ^{13}C NMR (DEPT, 75.5 MHz, C_6D_6): δ=137.6 (C), 136.9 (C), 135.2 (CH), 128.6 (CH), 128.2 (CH), 127.7 (CH), 127.2 (CH), 126.5 (CH), 86.7 (C), 69.4 (CH), 51.5 (CH_3), 46.2 (CH), 43.5 (CH_2), 23.7 (CH_3), 22.6 (CH_3), 17.1 ppm (CH_3); HRMS (70 eV, EI): m/z: calcd for $C_{21}H_{31}NO$: 313.2406 [M^+]; found: 313.2413.

(1*R,5*R**)-5-[(*E*)-(2-Furyl)ethenyl]-*N*,*N*-diisopropyl-5-methoxy-3-methyl-2-cyclopentenamine (6c)**: Aminodiene **2b** (84 mg, 0.5 mmol) and carbene complex **5b** (184 mg, 0.4 mmol) afforded **6c** (104 mg, 86%, 60% *de* in Et_2O; 97 mg, 80%, 80% *de* in THF) as a colorless oil. R_f: 0.20 (hexane/

ethyl acetate 5:1); ^{1}H NMR (300 MHz, C_6D_6): δ = 7.03 (d, J = 1.8 Hz, 1H; =CHO), 6.54 (d, J = 16.4 Hz, 1H; 2-FuC*H*=CH), 6.37 (d, J = 16.4 Hz, 1H; 2-FuCH=C*H*), 6.08 (dd, J = 3.3, 1.8 Hz, 1H; C*H*=CHO), 6.02 (d, J = 3.3 Hz, 1H; C*H*CH=CHO), 5.29 (brs, 1H; MeC=C*H*), 3.81 (brs, 1H; =CCHN), 3.15 (heptet, J = 6.7 Hz, 2H; 2×N(C*H*Me), 3.15 (s, 3H; OMe), 2.49 (d, J = 16.4 Hz, 1H; C*H*H), 2.09 (d, J = 16.4 Hz, 1H; CH*H*), 1.60 (s, 3H; MeC=), 1.19 (d, J = 6.7 Hz, 6H; 2×N(CH*Me*Me), 1.01 (d, J = 6.7 Hz, 6H; 2×N(CHMe*Me*); ^{13}C NMR (DEPT, 75.5 MHz, C_6D_6): δ = 153.3 (C), 141.5 (CH), 136.9 (C), 134.5 (CH), 128.1 (CH), 116.7 (CH), 111.3 (CH), 107.2 (CH), 86.2 (C), 69.4 (CH), 51.6 (CH_3), 46.0 (CH), 43.9 (CH_2), 23.5 (CH_3), 22.7 (CH_3), 17.0 ppm (CH_3); HRMS (70 eV, EI): m/z: calcd for $C_{19}H_{29}NO_2$: 303.2198 [M^+]; found: 303.2203.

(1*R,5*S**)-5-[(*E*)-(2-Furyl)ethenyl]-*N*,*N*-diisopropyl-5-methoxy-3-methyl-2-cyclopentenamine diast-(6c)**: R_f: 0.50 (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, C_6D_6): δ = 7.14 (d, J = 1.8 Hz, 1H; =CHO), 6.73 (d, J = 16.6 Hz, 1H; 2-FuC*H*=CH), 6.42 (d, J = 16.6 Hz, 1H; 2-FuCH=C*H*), 6.23–6.15 (m, 2H; C*H*=CHO, C*H*CH=CHO), 5.49 (brs, 1H; MeC=C*H*), 4.33 (brs, 1H; =CCHN), 3.20 (s, 3H; OMe), 2.92 (heptet, J = 6.5 Hz, 2H; 2×NC*H*Me, 2.41 (s, 2H; CH_2), 1.76 (s, 3H; MeC=), 1.22 (d, J = 6.5 Hz, 6H; 2×NCH*Me*Me), 1.03 ppm (d, J = 6.5 Hz, 6H; NCHMe*Me*); ^{13}C NMR (DEPT, 75.5 MHz, C_6D_6): δ = 153.6 (C), 141.8 (CH), 137.5 (C), 132.2 (CH), 128.6 (CH), 118.4 (CH), 111.2 (CH), 107.0 (CH), 89.3 (C), 72.4 (CH), 50.6 (CH_3), 45.9 (CH), 41.5 (CH_2), 23.5 (CH_3), 22.1 (CH_3), 15.7 ppm (CH_3); HRMS (70 eV, EI): m/z: calcd for $C_{19}H_{29}NO_2$: 303.2198 [M^+]; found: 303.2187.

(1*R,5*R**)-*N*,*N*-Diisopropyl-5-methoxy-2-methyl-5-[(*E*)-styryl]-2-cyclopentenamine (6d)**: Aminodiene **2c** (84 mg, 0.5 mmol) and carbene complex **5a** (188 mg, 0.4 mmol) afforded **6d** (92 mg, 73%, >95% *de*) as a colorless oil. R_f: 0.36 (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, C_6D_6): δ = 7.29–7.04 (m, 5H; ArH), 6.51 (d, J = 16.4 Hz, 1H; PhC*H*=CH), 6.35 (d, J = 16.4 Hz, 1H; PhCH=C*H*), 5.40–5.36 (m, 1H; MeC=C*H*), 3.54 (s, 1H; =CCHN), 3.21–2.97 (m, 2H; 2×NC*H*Me), 3.11 (s, 3H; OMe), 2.45–2.21 (m, 2H; CH_2), 1.70 (d, J = 1.6 Hz, 3H; =CMe), 1.29 (d, J = 6.7 Hz, 6H; 2×NCH*Me*Me), 1.02 ppm (d, J = 6.7 Hz, 6H; 2×NCHMe*Me*); ^{13}C NMR (DEPT, 75.5 MHz, C_6D_6): δ = 141.0 (C), 137.6 (CH), 135.9 (CH), 128.6 (CH), 127.3 (CH), 127.1 (CH), 126.4 (CH), 123.1 (CH), 84.3 (C), 72.4 (CH), 51.3 (CH_3), 48.1 (br; CH), 44.7 (br; CH), 39.4 (CH_2), 24.9 (br; CH_3), 23.0 (br; CH_3), 15.7 ppm (CH_3); HRMS (70 eV, EI): m/z: calcd for $C_{21}H_{31}NO$: 313.2406 [M^+]; found: 313.2415.

(1*R,5*R**)-5-[(*E*)-(2-Furyl)ethenyl]-*N*,*N*-diisopropyl-5-methoxy-2-methyl-2-cyclopentenamine (6e)**: Aminodiene **2b** (84 mg, 0.5 mmol) and carbene complex **5b** (184 mg, 0.4 mmol) afforded **6e** (86 mg, 71%, 80% de) as a colorless oil. R_f: 0.36 (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, C_6D_6): δ = 7.00 (d, J = 1.6 Hz, 1H; =CHO), 6.54 (d, J = 16.0 Hz, 1H; 2-FuC*H*=CH), 6.37 (d, J = 16.0 Hz, 1H; 2-FuCH=C*H*), 6.07 (dd, J = 3.5, 1.6 Hz, 1H; C*H*=CHO), 5.97 (d, J = 3.5 Hz, 1H; C*H*CH=CHO), 5.33–5.29 (m, 1H; MeC=C*H*), 3.52 (brs, 1H; =CCHN), 3.20–2.90 (m, 2H; 2×NC*H*Me), 3.09 (s, 3H; OMe), 2.36 (brd, J = 16.0 Hz, 1H; C*H*H), 2.19 (app.d, J = 16.0 Hz, 1H; CH*H*), 1.64 (d, J = 1.5 Hz, 3H; Me), 1.24 (d, J = 6.3 Hz, 6H; 2×NCH*Me*Me), 0.98 ppm (d, J = 6.7 Hz, 6H; 2×NCHMe*Me*); ^{13}C NMR (DEPT, 75.5 MHz, C_6D_6): δ = 153.3 (C), 141.4 (CH), 141.0 (C), 135.2 (CH), 123.0 (CH), 115.9 (CH), 111.3 (CH), 107.1 (CH), 84.1 (C), 72.4 (CH), 51.3 (CH_3), 47.9 (br; CH), 44.6 (br; CH), 39.4 (CH_2), 24.8 (br; CH_3), 23.1 (br; CH_3), 15.7 ppm (CH_3); HRMS (70 eV, EI): m/z: calcd for $C_{19}H_{29}NO_2$: 303.2198 [M^+]; found: 303.2204.

2-{(4a*S,5*S**)-2,3,4,4a,5,6-Hexahydro-7-methoxycyclopenta[*b*]pyran-5-yl}ethanal (8a)**: Aminodiene **2a** (77 mg, 0.5 mmol) and carbene complex **7** (180 mg, 0.4 mmol) afforded **8a** (60 mg, 76%) as a colorless oil. R_f: 0.27 (hexane/ethyl acetate 5:1); ^{1}H NMR (600 MHz, C_6D_6): δ = 9.35 (t, J = 1.6 Hz, 1H; CHO), 3.85 (ddt, J = 10.6, 4.4, 1.7 Hz, 1H; C*H*HO), 3.81 (s, 3H; OMe), 3.27 (ddd, J = 12.9, 10.6, 2.3 Hz, 1H; CH*H*O), 2.47–2.43 (m, 1H; C*H*HCOMe), 2.05 (ddd, J = 15.7, 4.8, 1.6 Hz, 1H; C*H*HCH=O), 1.98–1.87 (m, 4H; CH*H*COMe, CH*H*CH=O, CHCO, C*H*CH$_2$CH=O), 1.75 (dqd, J = 12.9, 3.5, 1.7 Hz; 1H; C*H*HCHCO), 1.41 (qdd, J = 12.9, 4.4,3.6 Hz, 1H; C*H*HCH$_2$CH$_2$O), 1.24–1.19 (m, 1H; CH*H*CH$_2$CH$_2$O), 0.92 ppm (qd, J = 12.9, 3.6, 1H; CH*H*CHCO); ^{13}C NMR (DEPT, 150 MHz, C_6D_6): δ = 200.1 (CH), 132.9 (C), 129.5 (C), 68.7 (CH_2), 57.5 (CH_3), 48.6 (CH_2), 43.9 (CH), 34.8 (CH_2), 34.1 (CH), 30.9 (CH_2), 24.9 ppm (CH_2); HRMS (70 eV, EI): m/z: calcd for $C_{11}H_{16}O_3$: 196.1099 [M^+]; found: 196.1105.

2-{(4a*S,5*S**)-2,3,4,4a,5,6-Hexahydro-7-methoxycyclopenta[*b*]pyran-5-yl}propanal (8b)**: Aminodiene **2b** (84 mg, 0.5 mmol) and carbene complex **7** (180 mg, 0.4 mmol) afforded **8b** (66 mg, 79%, 1:1 mixture of diastereoisomers) as a colorless oil. R_f: 0.30 (hexane/ethyl acetate 5:1); ^{1}H NMR (200 MHz, C_6D_6): δ = 9.29, 9.28 (2s, 2H; 2×CHO), 3.90–3.70 (m, 2H; 2×C*H*HO), 3.86 (s, 6H; 2×OMe), 3.21 (app.ddd, J = 12.8, 10.5, 2.3 Hz, 2H; 2×CH*H*O), 2.20–0.80 (m, 18H; 2×C*H*$_2$C*H*$_2$C*H*CH-(C*H*$_2$)C*H*Me), 0.72, 0.69 ppm (2×d, J = 6.9 Hz, 6H; 2×Me); ^{13}C NMR (DEPT, 100 MHz, C_6D_6): δ = 202.9 (CH), 202.6 (CH), 133.0 (C), 132.9 (C), 129.4 (C), 68.8 (CH_2), 57.5 (CH_3), 57.5 (CH_3), 50.2 (CH), 50.1 (CH), 41.9 (CH), 41.2 (CH), 40.3 (CH), 40.0 (CH), 33.0 (CH_2), 32.3 (CH_2), 31.7 (CH_2), 31.6 (CH_2), 25.0 (CH_2), 25.0 (CH_2), 11.1 (CH_3), 11.0 ppm (CH_3).

(4a*S,5*R**)-2,3,4,4a,5,8-Hexahydro-*N*,*N*-diisopropyl-9-methoxy-7-methyl-cyclohepta[*b*]pyran-5-amine (9)**: Aminodiene **2c** (84 mg, 0.5 mmol) and carbene complex **7** (180 mg, 0.4 mmol) afforded **9** (81 mg, 69%) as a colorless oil. R_f: 0.52 (hexane/ethyl acetate 5:1); ^{1}H NMR (400 MHz, C_6D_6): δ = 5.57 (brs, 1H; CH=), 3.83–3.70 (m, 2H; CH_2O), 3.68 (s, 3H; OMe), 3.39 (d, J = 17.4 Hz, 1H; C*H*HCMe), 3.38–3.26 (m, 3H; =CCHN, 2×NC*H*Me), 2.66–2.48 (m, 1H; C*H*CHN), 2.41 (d, J = 17.4 Hz, 1H; CH*H*CMe), 1.86 (s, 3H; Me), 1.85–1.60 (m, 3H; C*H*$_2$CH$_2$O, C*H*HCH), 1.60–1.45 (m, 1H; CH*H*CH), 1.14 (d, J = 6.8 Hz, 6H; 2×NCH*Me*Me), 1.03 ppm (d, J = 6.5 Hz, 6H; 2×NCHMe*Me*); ^{13}C NMR (DEPT, 100 MHz, C_6D_6): δ = 138.9 (C), 133.8 (C), 128.2 (CH), 127.7 (CH), 68.6 (CH_2), 58.6 (CH_3), 54.6 (CH), 46.6 (CH), 42.1 (CH), 35.2 (CH_2), 26.6 (CH_3), 24.8 (CH_2), 24.4 (CH_2), 23.9 (CH_3), 21.8 ppm (CH_3); HRMS (70 eV, EI): m/z: calcd for $C_{18}H_{31}NO_2$: 293.2355 [M^+]; found: 293.2351.

Biphenyl-2-carbaldehyde (11a): Aminodiene **2a** (77 mg, 0.5 mmol) and carbene complex **10a** (134 mg, 0.4 mmol) afforded **11a** (48 mg, 66%) as a colorless oil. The analytical data are identical to those described in the literature.[24]

5-Methylbiphenyl-2-carbaldehyde (11b): Aminodiene **2b** (84 mg, 0.5 mmol) and carbene complex **10a** (134 mg, 0.4 mmol) afforded **11b** (55 mg, 70%) as a colorless oil. R_f: 0.50 (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.98 (s, 1H; CHO), 7.99 (d, J = 8.0 Hz, 1H; ArH), 7.51–7.33 (m, 6H; ArH), 7.30 (s, 1H; ArH), 2.50 ppm (s, 3H; Me); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 192.0 (CH), 146.0 (C), 144.4 (C), 137.8 (C), 131.4 (C), 131.2 (CH), 129.9 (CH), 128.5 (CH), 128.2 (CH), 127.9 (CH), 127.5 (CH), 21.7 ppm (CH_3).

4-Methylbiphenyl-2-carbaldehyde (11c): Aminodiene **2c** (84 mg, 0.5 mmol) and carbene complex **10a** (134 mg, 0.4 mmol) afforded **11c** (57 mg, 72%) as a colorless oil. R_f: 0.50 (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.00 (s, 1H; CHO), 7.89 (s, 1H; ArH), 7.57–7.26 (m, 7H; ArH), 2.49 ppm (s, 3H; Me); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 192.6 (CH), 139.9 (C), 137.8 (C), 137.6 (C), 134.3 (CH), 133.4 (C), 130.6 (CH), 130.0 (CH), 128.2 (CH), 127.8 (CH), 127.6 (CH), 20.9 ppm (CH_3).

1,2,3,4-Tetrahydro-9-methoxy-6-methyl-4*H*-fluorene (12a): Aminodiene **2b** (84 mg, 0.5 mmol) and carbene complex **10c** (136 mg, 0.4 mmol) afforded **12b** (52 mg, 61%) as a colorless oil. R_f: 0.58 (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72 (d, J = 7.8 Hz, 1H; ArH), 7.32 (d, J = 7.8 Hz, 1H; ArH), 6.96 (s, 1H; ArH), 4.88 (s, 1H; OCH), 3.07 (s, 3H; OMe), 2.40 (s, 3H; MeC), 1.83–1.62 ppm (m, 8H; aliphatic ring); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 137.9 (C), 137.0 (C), 136.6 (C), 130.2 (C), 127.4 (C), 125.2 (CH), 123.2 (CH), 118.6 (CH), 83.5 (CH), 51.9 (CH_3), 29.6 (CH_2), 23.4 (CH_2), 22.7 (CH_2), 22.3 (CH_2), 21.5 ppm (CH_3).

3-Methoxy-2-phenyl-1*H*-indene (12b): Aminodiene **2a** (77 mg, 0.5 mmol) and carbene complex **10d** (145 mg, 0.4 mmol) afforded **12c** (49 mg, 55%) as a colorless oil. R_f: 0.51 (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (d, J = 8.3 Hz, 1H; ArH), 7.51–7.13 (m, 8H; ArH), 3.97 (s, 3H; OMe), 3.66 ppm (s, 2H; CH_2); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 141.1 (C), 140.8 (C), 135.2 (C), 128.3 (CH), 128.0 (C), 126.7 (CH), 126.5 (CH), 126.3 (CH), 125.3 (CH), 124.6 (C), 123.9 (CH), 118.5 (CH), 58.8 (CH_3), 36.1 ppm (CH_2).

Acknowledgements

This research was supported by the DGICYT (CTQ2004–08077-C02-01/BQU). M.F.-M is indebt to the MEC (predoctoral grant). Many thanks are due to Dr. E. Rubio and Dr. I. Merino for helping in the NMR structural elucidation.

[1] a) T. Hudlicky, J. D. Price, *Chem. Rev.* **1989**, *89*, 1467–1486; b) R. D. Little in *Comprehensive Organic Synthesis, Vol. 5* (Eds.: M. Trost, I. Fleming), Pergamon Press, Oxford, **1991**, *Chapter 3.1B*, pp. 239–270; c) D. M. T. Chan in *Comprehensive Organic Synthesis, Vol. 5* (Eds.: M. Trost, I. Fleming), *Chapter 3.2*, pp. 271–314; d) S. E. Denmark in *Comprehensive Organic Synthesis, Vol. 5* (Eds.: M. Trost, I. Fleming), *Chapter 6.3*, pp. 751–784; e) M. Lautens, W. Klute, W. Tam, *Chem. Rev.* **1996**, *96*, 49–92.

[2] a) T. L. Ho *Carbocycle Construction in Terpene Synthesis*, Wiley-VCH, New York, **1988**; b) T. Hudlicky, F. Rulin, T. C. Lovelace, J. W. Reed in *Studies in Natural Products Chemistry* (Ed.: T., Attaur-Rahman), Elsevier Science, Essex, U.K., **1989**.

[3] H.-W. Frühauf, *Chem. Rev.* **1997**, *97*, 523–526.

[4] For recent reviews see: a) K. H. Dötz, P. Tomuschat, *Chem. Soc. Rev.* **1999**, *28*, 187–198; b) J. W. Herndon, *Tetrahedron*, **2000**, *56*, 1257–1280; c) A. de Meijere, H. Schirmer, M. Duetsch, *Angew. Chem.* **2000**, *112*, 4124–4162; *Angew. Chem. Int. Ed.* **2000**, *39*, 3964–4002; d) M. A. Sierra, *Chem. Rev.* **2000**, *100*, 3591–3637; e) J. Barluenga, F. J. Fañanás, *Tetrahedron* **2000**, *56*, 4597–4628; f) J. Barluenga, J. Flórez, F. J. Fañanás, *J. Organomet. Chem.* **2001**, *624*, 5–17; g) J. Barluenga, *Pure Appl. Chem.* **2002**, *74*, 1317–1325; h) J. Barluenga, M. Tomás, J. Santamaría, *Chem. Rev.* **2004**, *104*, 2259–2283; i) *Metal Carbenes in Organic Synthesis, Topics Organomet. Chem.* (Ed.: K. H. Dötz), *Vol. 13*, Springer, Berlin, **2004**; j) J. Barluenga, M. A. Fernández-Rodriguez, E. Aguilar, *J. Organomet. Chem.* **2005**, *690*, 539–587; k) Y.-T. Wu, T. Kurahashi, A. de Meijere, *J. Organomet. Chem.* **2005**, *690*, 5900–5911; l) J. Barluenga, S. Martínez, *Arkivoc* **2006**, 129–147; m) M. A. Sierra, M. Gómez-Gallego, R. Martínez-Álvarez, *Chem. Eur. J.* **2007**, *13*, 736–744.

[5] a) W. D. Wulff in *Comprehensive Organometallic Chemistry II, Vol. 12* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, pp. 469–547; b) J. Barluenga, F. Rodríguez, F. J. Fañanás, J. Flórez in *Metal Carbenes in Organic Synthesis, Topics Organomet. Chem., Vol 13* (Ed.: K. H. Dötz), Springer, Berlin, **2004**, pp. 59–121.

[6] J. Barluenga, F. Aznar, M. Fernández, *Chem. Eur. J.* **1997**, *3*, 1629–1637.

[7] J. Barluenga, A. Ballesteros, J. Santamaría, M. Tomás, *J. Organomet. Chem.* **2002**, *643–644*, 363–368.

[8] J. Barluenga, F. Aznar, A. Martín, *Organometallics* **1995**, *14*, 1429–1433.

[9] a) J. Barluenga, R. M. Canteli, J. Flórez, S. García Granda, A. Gutiérrez-Rodríguez, *J. Am. Chem. Soc.* **1994**, *116*, 6949–6950; b) J. Barluenga, R. M. Canteli, J. Flórez, S. García Granda, A. Gutiérrez-Rodríguez, E. Martín, *J. Am. Chem. Soc.* **1998**, *120*, 2514–2522.

[10] a) J. Barluenga, F. Aznar, A. Martín, S. Barluenga, S. García-Granda, A. A. Paneque-Quevedo, *J. Chem. Soc. Chem. Commun.* **1994**, 843–844; b) J. Barluenga, F. Aznar, A. Martín, S. Barluenga, *Tetrahedron* **1997**, *53*, 9323–9340.

[11] a) J. Barluenga, F. Aznar, A. Martín, S. García-Granda, M. A. Salvadó, P. Pertierra, *J. Chem. Soc. Chem. Commun.* **1993**, 319–321; b) J. Barluenga, F. Aznar, A. Martín, J. T. Vázquez, *J. Am. Chem. Soc.* **1995**, *117*, 9419–9426.

[12] a) J. Barluenga, M. Tomás, A. Ballesteros, J. Santamaría, R. J. Carbajo, F. López-Ortiz, *Chem. Eur. J.* **1996**, *2*, 88–97; b) J. Barluenga, M. Tomás, A. Ballesteros, J. Santamaría, R. Corzo-Suárez, S. García-Granda, *New J. Chem.* **2001**, *25*, 8–10.

[13] J. Barluenga, M. Tomás, E. Rubio, J. A. López-Pelegrin, S. García-Granda, M. Pérez-Priede, *J. Am. Chem. Soc.* **1999**, *121*, 3065–3071.

[14] a) J. Barluenga, F. Aznar, S. Barluenga, *J. Chem. Soc. Chem. Commun.* **1995**, 1973–1974; b) J. Barluenga, F. Aznar, S. Barluenga, A. Martín, S. García-Granda, E. Martín, *Synlett* **1998**, 473–474; c) J. Barluenga, F. Aznar, S. Barluenga, M. Fernández, A. Martín, S. García-Granda, A. Piñera-Nicolás, *Chem. Eur. J.* **1998**, *4*, 2280–2298.

[15] The substitution pattern has been shown to play an important role on the reactivity of alkenyl carbene complexes and methyl ketone lithium enolates. See for example: a) J. Barluenga, J. Alonso, F. J. Fañanás, *J. Am. Chem. Soc.* **2003**, *125*, 2610–2616; b) J. Barluenga, J. Alonso, F. J. Fañanás, *Chem. Eur. J.* **2005**, *11*, 5397–5407.

[16] For 1,3-metal migrations see: a) H. F. Sleiman, L. McElwee-White, *J. Am. Chem. Soc.* **1988**, *110*, 8700–8701; b) L. S. Hegedus, B. R. Lundmark, *J. Am. Chem. Soc.* **1989**, *111*, 9194–9198; c) C. T. Maxey, H. F. Sleiman, S. T. Massey, L. McElwee-White, *J. Am. Chem. Soc.* **1992**, *114*, 5153–5160; d) H. Fischer, A. Schlageter, W. Bidell, A. Früh, *Organometallics* **1991**, *10*, 389–391; e) J. Barluenga, M. Tomás, E. Rubio, J. A. López-Pelegrín, S. García-Granda, M. Pérez-Priede, *J. Am. Chem. Soc.* **1999**, *121*, 3065–3071.

[17] For 1,2-metal migrations see: a) H. Fischer, T. Meisner, J. Hofmann, *Chem. Ber.* **1990**, *123*, 1799–1804; b) K. H. Dötz, C. Christoffers, P. Knochel, *J. Organomet. Chem.* **1995**, *489*, C84–C86; c) J. Barluenga, M. Tomás, E. Rubio, J. A. López-Pelegrín, S. García-Granda, P. Pertierra, *J. Am. Chem. Soc.* **1996**, *118*, 695–696; d) N. Iwasawa, K. Maeyama, M. Saitou, *J. Am. Chem. Soc.* **1997**, *119*, 1486–1487; e) N. Iwasawa, K. Maeyama, *J. Org. Chem.* **1997**, *62*, 1918–1919; f) N. Iwasawa, T. Ochiai, K. Maeyama, *Organometallics*, **1997**, *16*, 5137–5139; g) N. Iwasawa, T. Ochiai, K. Maeyama, *J. Org. Chem.* **1998**, *63*, 3164–3165; h) J. Barluenga, E. Rubio, J. A. López-Pelegrín, M. Tomás, *Angew. Chem.* **1999**, *111*, 1163–1165; *Angew. Chem. Int. Ed.* **1999**, *38*, 1091–1093.

[18] E. O. Fischer, G. C. Kreiter, H. J. Kollmeier, J. Müller, R. D. Fischer, *J. Organomet. Chem.* **1971**, *28*, 237–258.

[19] J. S. McCallum, F. A. Kunng, S. C. Gilbertson, W. D. Wulff, *Organometallics* **1988**, *7*, 2346–2360.

[20] R. Aumann, H. Heinen, *Chem. Ber.* **1987**, *120*, 537–540.

[21] K. S. Chan, G. A. Peterson, T. A. Brandvold, K. l. Faron, C. A. Challener, C. Hyldahl, W. D. Wulf, *J. Organomet. Chem.* **1987**, *334*, 9–56.

[22] C. A. Merlic, D. Xu, *J. Am. Chem. Soc.* **1991**, *113*, 7418–7420.

[23] J. Barluenga, F. Aznar, M. A. Palomero, S. Barluenga, *Org. Lett.* **1999**, *1*, 541–544.

[24] a) G. Cahiez, F. Lepifre, P. Ramiandrosoa, *Synthesis* **1999**, 2138–2144; b) J. A. Varela, D. Peña, B. Goldfuss, D. Denisenko, J. Kulhanek, K. Polborn, P. Knochel, *Chem. Eur. J.* **2004**, *10*, 4252–4264; c) T. Inokuchi, H. Kawafuchi, *Tetrahedron* **2004**, *60*, 11969–11975.

Received: July 18, 2007
Published online: September 21, 2007

