Cyclic BF_2 Adducts of Functionalized Fischer Vinylcarbene Complexes: Preparation and Stereoselective Diels−Alder Reactions with 2-Amino 1,3-Dienes

José Barluenga,*,† Rosa-María Canteli,† Josefa Flórez,† Santiago García-Granda,‡ Angel Gutiérrez-Rodríguez,‡ and Eduardo Martín‡

Contribution from the Instituto Universitario de Química Organometálica "Enrique Moles", Unidad Asociada al CSIC, and Departamento de Química Física y Analítica, Universidad de Oviedo, Julián Clavería 8, 33071 Oviedo, Spain

Received July 29, 1997

Abstract: A new type of cyclic amino-functionalized s-cis boroxyvinylcarbene complex of group 6 metals has been synthesized. These complexes underwent Diels−Alder-type reactions with 2-amino 1,3-dienes that proceeded with complete regioselectivity and high exo or endo diastereoselectivity, which was found to be highly dependent on the nature of the substituents on the diene. When chiral 2-amino-5-alkoxy dienes derived from (*S*)-prolinol benzyl or methyl ether were used, an exclusive exo and highly diastereofacially selective [4 + 2] cycloaddition was achieved, affording spiro carbene complexes with three contiguous stereogenic centers and a high level of enantiomeric purity. Removal of the $Cr(CO)_5$ fragment and the BF_2 group provided an entry to α,α-branched *β*-amino aldehydes or *β*-amino acids. In addition, the stable form of an amino-substituted hydroxycarbene complex of chromium was characterized by X-ray diffraction.

Introduction

Heteroatom-stabilized transition-metal carbene complexes (Fischer-type) have turned out to be important stoichiometric or catalytic reagents for the transformation of organic substrates.[1] Of the many systems that are currently accessible, group 6 metal alkoxy-[2] and aminocarbene[3] derivatives are among the most widely used Fischer carbene complexes. Nevertheless, boroxy-,[4] siloxy-,[5] and other metaloxycarbene[6] (metal = Ti,[7] Zr,[8] Hf,[9] Th[10]) complexes have been prepared, although their chemistry has been much less explored. So far, the only known group 6 boroxy derivatives are the dialkylboroxycarbene complexes **1**[4a] and **2**,[4b] which have been prepared following Fischer's original procedure and either characterized or isolated at temperatures below −20 or 0 °C due to their thermal instability (Chart 1). The known examples of group 6 cyclic heterobimetallic functionalized Fischer carbene compounds are the nine-membered zirconoxycarbene complexes **3**[11] and the five-membered metallatricyclic zirconoxycarbene complexes **4**,[8f] which were prepared by successive treatment of (η^4-butadiene)-zirconocene with a hexacarbonylmetal and a carbonyl (ketone or aldehyde) substrate in the former case or by reaction of (η^2-formaldehyde)zirconocene dimer with a metal carbonyl complex in the latter one. In addition, the nitrogen-containing nine-membered metaloxycarbene complexes of vanadium **5** have

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‡ Departamento de Química Física y Analítica. X-ray crystal structure analyses.

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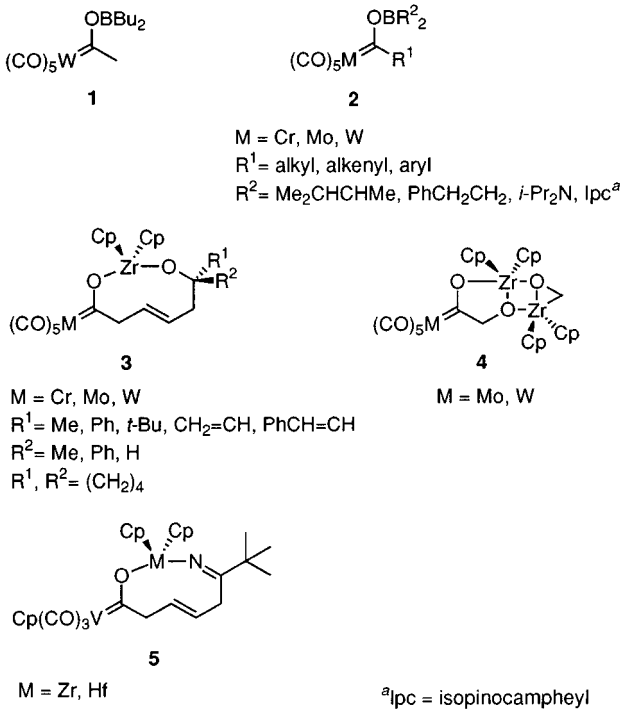
S0002-7863(97)02588-2 CCC: $15.00
Published on Web 03/10/1998

Chart 1



been reported and analogously prepared from the corresponding (butadiene)metallocene, (cyclopentadienyltetracarbonyl)vanadium, and pivalonitrile.[12] On the other hand, group 6 hydroxycarbene complexes are thermally unstable and decompose rapidly at room temperature to the corresponding aldehyde[13] or by a metal carbonyl producing C−C bond cleavage.[11b] Due to their lability, this type of carbene complex is prepared only in situ,[8g,14] although a few examples have been isolated at low temperature.[15]

Given the strong electron-withdrawing property of the pentacarbonylmetal group, Fischer alkenylcarbene complexes behave as exceptionally reactive, regioselective, and mainly endo-diastereoselective dienophiles in Diels−Alder reactions.[2b,16] The first studied alkoxyalkenylcarbene derivatives, which are assumed to react in an s-trans conformation, led to different endo/exo product ratios, in which the former is usually the major isomer.[17,18] In contrast, the less reactive aminoalkenylcarbene complexes, which are assumed to react in an s-cis conformation of the vinylcarbene unit, gave the exo cycloadducts with high selectivity.[19] It is well-recognized that the Diels−Alder reaction, a valuable and widely used synthetic tool, is generally an endo-selective cycloaddition.[20] However, exo selectivity seems to be a general property of conformationally restricted s-cis dienophiles.[21] In addition, there are some cases of exo-selective Diels−Alder additions with α-substituted dienophiles[22] and other substrate-specific examples.[23]

In this paper, we provide full details of the synthesis of novel boroxyvinylcarbene complexes with a cyclic chelate structure, which temporarily fixes the s-cis conformation of the exocyclic carbon−carbon and carbon−chromium double bonds. We also describe the diastereoselective Diels−Alder-type reactions of these boron difluoride complexes with 2-amino 1,3-dienes, which take place with high exo- or endo-selectivity depending on the substitution pattern of the diene. In addition, we report on a highly asymmetric and exo-selective Diels−Alder reaction of the above complexes with chiral 2-amino 1,3-dienes.[24]

Results and Discussion

Preparation of Chelate Boroxycarbene Complexes 7. The new carbene complexes **7** were synthesized from the corresponding (2-bromoallyl)amines **6** as shown in Scheme 1. Treatment of the appropriate amine **6** with *tert*-butyllithium led to the corresponding *β*-amino-functionalized vinylic organolithium compound,[25] which subsequently was added to an ethereal solution of the corresponding group 6 metal hexacarbonyl. The lithium acylmetalate anions thus generated were then treated with an excess of boron trifluoride etherate, affording carbene complexes **7**, which after silica gel column

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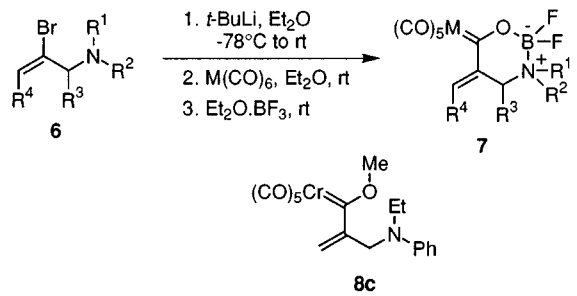
Scheme 1



chromatography were isolated as dark-red solids that are perfectly stable in the solid state and can be stored under nitrogen for several months, though they very slowly decomposed upon standing (2−5 days) at room temperature in THF or CH_2Cl_2 solutions. The chromium and tungsten derivatives **7a**−**g**,**i** were obtained with moderate yields (Table 1), but in the case of the molybdenum compound **7h** the yield was very low (Table 1, entry 8), presumably due to the relative instability of molybdenum carbene complexes.[26] The structures of these complexes **7** were determined from their spectral data and unambiguously established by single-crystal X-ray diffraction of compounds **7a** and **7c**,[24] which showed the formation of a six-membered ring oxazaboracycle that locked the vinylcarbene complex into an s-cis conformation.[27,28] Actually, the formation of these BF_2-chelated adducts **7** was unexpectedly observed when following Fischer's original procedure; alkylation of the lithium acylate intermediate was carried out with triethyloxonium tetrafluoroborate. On the other hand, the conventional and initially expected *O*-methylated *β*-nitrogen-functionalized carbene complex **8c** (Scheme 1) was obtained (31% yield) using methyl triflate as alkylating agent.

In the course of these studies we accidentally found that silica gel flash column chromatography of the lithium acylmetalate salt, generated after successive treatment of (2-bromoallyl)amine **6b** with *t*-BuLi and $Cr(CO)_6$, gave a stable orange solid whose structure, tentatively assigned as a hydroxyvinylcarbene complex from the NMR data, was finally ascertained to be the intramolecular ammonium salt **9** by an X-ray crystallographic study[29] (Scheme 2). This dipolar structure **9**, which presents an intramolecular hydrogen bond, is apparently the stable form of the originally formed hydroxycarbene complex as a consequence of the presence of both an acidic (hydroxycarbene) and a basic group (aliphatic amine) in the molecule.

Diels−Alder Reactions of Complexes 7 with 2-Amino 1,3-Dienes.[30] We first studied the reaction of carbene complex **7a** with 2-amino-3-methylbutadiene **10** (Scheme 3). These products were mixed in THF at −78 °C, and the mixture was slowly warmed to room temperature overnight. The end of the reaction is clearly shown by a color change from dark red due to the α,*β*-unsaturated nature of the starting carbene complex **7a** to orange-yellow characteristic of saturated or nonconjugated Fischer carbene complexes. After silica gel chromatographic purification only one regioisomeric cycloadduct **11**, in agreement with the polarization of diene and dienophile, was isolated as a yellow solid. Subsequent acid hydrolysis of the enamine group afforded spiro carbene complex **12** as a single diastereoisomer. The reaction under the same experimental conditions of complex **7a** with 2-amino diene **13**, which has the nonenaminic C−C double bond inside a six-membered ring, analogously led to only one regio- and diastereoisomeric adduct **14** (chromatographic purification was performed in this case on basic aluminum oxide). Acid hydrolysis of **14** gave exclusively tricyclic carbene complex *rac*-**15**. The experiments with 2-amino dienes **16** and **17** derived from an aliphatic amine led to similar results. Treatment of **7a** with **16** under the above conditions, where hydrolysis of the more labile aliphatic enamine group took place, provided directly ketocarbene complex **18** as a unique isomer. By contrast, in the reaction of **7a** with **17** enamino carbene complex **19** was isolated. This product is the result of a [4 + 2] cycloaddition followed by isomerization of the enaminic C−C double bond[31] and was easily transformed to compound *rac*-**15** under acidic conditions. The stereochemistry shown for compounds in Scheme 3 has been assumed by analogy from subsequent results and corresponds to an exo diene−dienophile orientation. The relative configuration of the third generated stereogenic carbon at the position α to the carbonyl group of compound **18** has not been determined.

Next we examined the reactions of racemic carbene complex **7c** containing a stereogenic nitrogen atom with aromatic 2-amino dienes **10** and **13**, and the results are shown in Scheme 4. In the first case, the [4 + 2] cycloaddition of **7c** with diene **10** yielded, after basic aluminum oxide column chromatography, a 3:1 mixture of spiro enamino carbene complexes **20a**:**20b**. These diastereoisomers differ in the relative configuration of the stereogenic nitrogen and spiranic carbon atoms. A similar behavior was observed in the reaction of **7c** with **13**, which provided a mixture of three isomers **21a**,**a′**,**b** from which complex **21b** was separated by silica gel column chromatography. The major fraction was a mixture of isomers **21a**,**a′**, which differ in the position of the enaminic C−C double bond and which could not be separated by the above procedure. Therefore, this mixture was transformed to a single diastereoisomer **22** by acid hydrolysis of the enamine group. A single-crystal X-ray analysis of compound **22**[32] confirmed the structure and unambiguously established the stereochemistry as depicted in Scheme 4, which corresponds to a formal exo topology of

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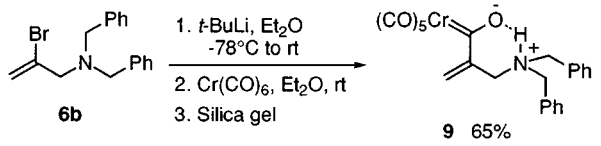
Table 1. Chelated Amino Functionalized Boroxyalkenylcarbene Complexes **7**

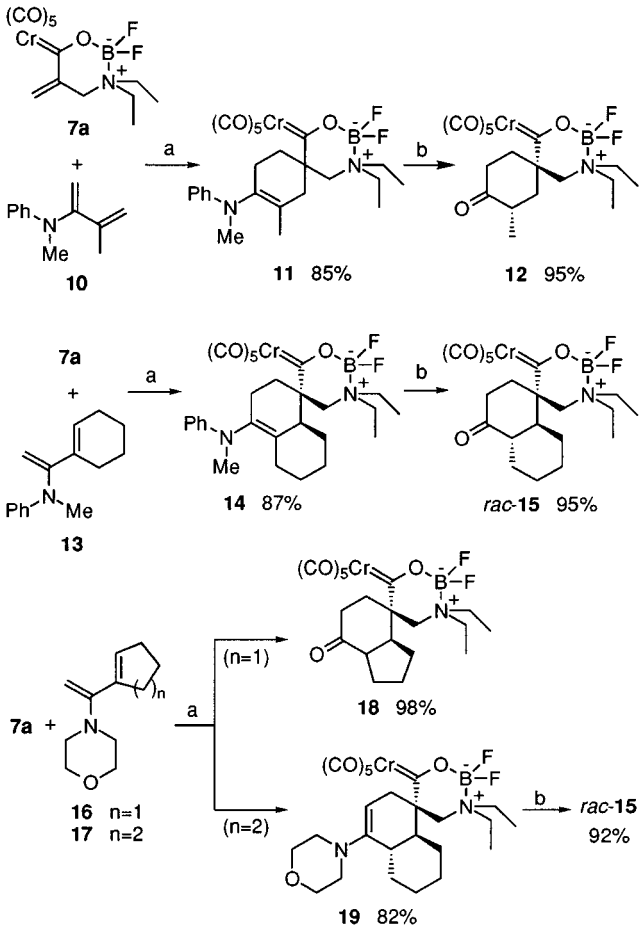
entry	starting material	R^1	R^2	R^3	R^4	product	M	yield[a] (%)
1	**6a**	Et	Et	H	H	**7a**	Cr	39
2	**6b**	$PhCH_2$	$PhCH_2$	H	H	**7b**	Cr	34
3	**6c**	Et	Ph	H	H	**7c**	Cr	38
4	**6d**	Me	Ph	H	H	**7d**	Cr	35
5	**6e**	Me	*p*-Me_3CPh	H	H	**7e**	Cr	45
6	**6f**	Me	*p*-MeOPh	H	H	**7f**	Cr	33
7	**6g**	Et	Et	$-(CH_2)_3-$		**7g**	Cr	31
8	**6a**	Et	Et	H	H	**7h**	Mo	5
9	**6a**	Et	Et	H	H	**7i**	W	37

[a] Isolated yield based on the corresponding amine **6**.

Scheme 2



Scheme 3[a]

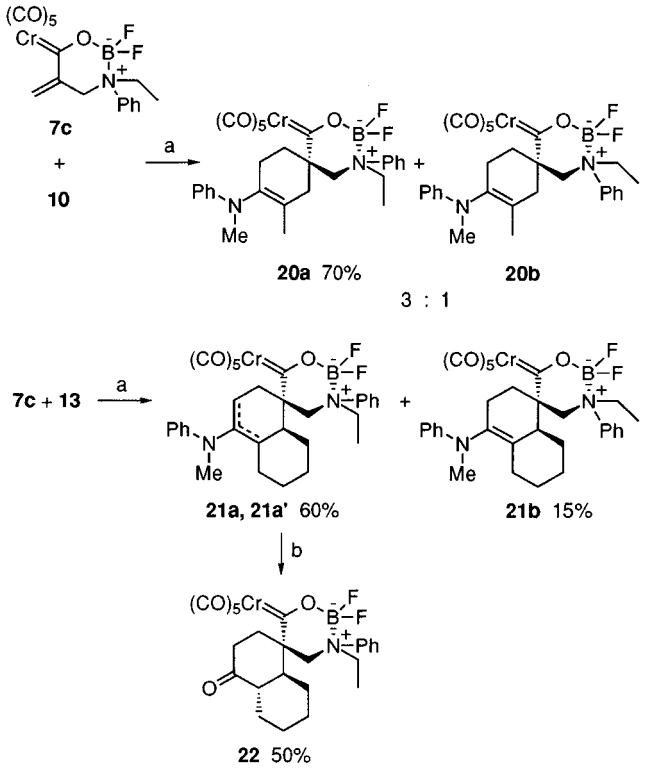


[a] Key: (a) (i) THF, −78 °C to rt, (ii) silica gel; (b) 3 N HCl, THF, rt.

diene and dienophile. In addition, it showed a *trans* fusion of the six-membered rings and a *cis* orientation of the *N*-ethyl substituent and the CH group bonded to the spiranic carbon.

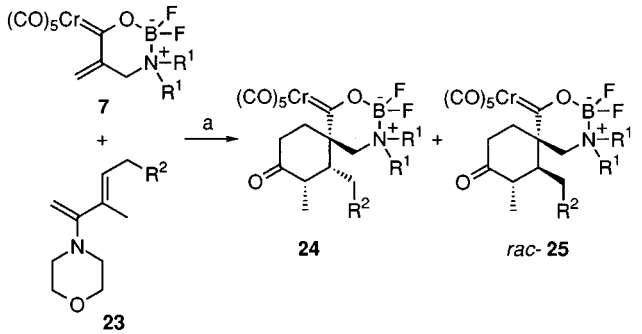
While the reactions of BF_2 chelate carbene complexes **7a** and **7c** with nonheteroatom 4-substituted 2-amino dienes **10**, **13**, **16**, and **17** afforded exclusively the corresponding exo cycloaddition products (Schemes 3 and 4), the reactions of the same carbene complexes with 2-morpholino dienes **23** bearing an alkoxy- or amino-containing group on the 4 position led to the corresponding ketocarbene complexes as a mixture of formal *endo*-**24** and

Scheme 4[a]



[a] Key: (a) (i) THF, −78 °C to rt, (ii) silica gel; (b) 3 N HCl, THF, rt.

Scheme 5[a]



[a] Key: (a) (i) THF, −78 °C to rt, (ii) silica gel.

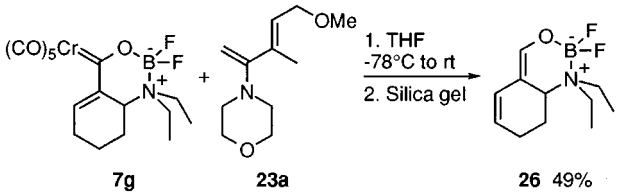
exo,rac-**25** Diels−Alder adducts in which the former is generally the major or even exclusive isomer isolated under otherwise analogous reaction conditions. These results are summarized in Scheme 5 and Table 2. Carbene complex **7a** reacted with alkoxy-substituted 2-morpholino dienes **23a**−**c** yielding the endo cycloadducts **24a**−**c** with high diastereomeric excess (Table 2, entries 1−3). The reactions of the same complex **7a** with propargyloxy-substituted amino diene **23d** and 2,5-diamino

Table 2. Preparation of Endo, Exo Cycloadducts **24** and *rac*-**25**, Respectively

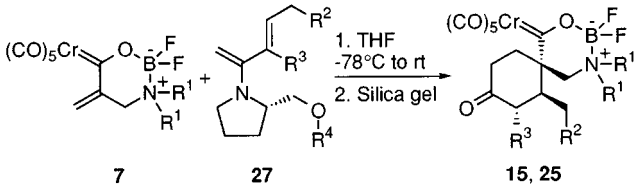
					endo			exo			
entry	complex **7**	R^1	diene **23**	R^2	product	yield[a] (%)	$\delta_{C=Cr}$[b] (ppm)	product	yield[a] (%)	$\delta_{C=Cr}$[b] (ppm)	de[c] (%)
1	**7a**	Et	**23a**	MeO	**24a**	56	381.2	*rac*-**25a**	3	365.2[d]	90
2	**7a**	Et	**23b**	$PhCH_2O$	**24b**	75	381.2[e]	*rac*-**25b**	7	366.4	83
3	**7a**	Et	**23c**	$CH_2{=}CHCH_2O$	**24c**	48	381.3	*rac*-**25c**	7	366.4	75
4	**7a**	Et	**23d**	$MeC{\equiv}CCH_2O$	**24d**	50	381.2	*rac*-**25d**	0	*f*	100
5	**7a**	Et	**23e**	Me_3SiO	**24e**	54	380.6[d]	*rac*-**25e**	18	366.5[e]	50
6	**7a**	Et	**23f**	PhMeN	**24f**	65	376.9	*rac*-**25f**	0	*f*	100
7	**7b**	$PhCH_2$	**23e**	Me_3SiO	**24g**	30	380.8	*rac*-**25g**	30	368.3	0

[a] Isolated yields based on the corresponding carbene complex **7**. [b] ^{13}C NMR chemical shift of the carbene carbon measured in CD_2Cl_2 at 75 MHz. [c] Diastereomeric excess determined from the amounts of isolated products. [d] Measurements carried out in $CDCl_3$. [e] Data recorded at 50 MHz. [f] Formation of the exo isomer was not observed.

Scheme 6



Scheme 7



diene **23f** afforded uniquely the corresponding endo isomers **24d** and **24f**, respectively (Table 2, entries 4 and 6). When the (trimethylsilyl)oxy-substituted amino diene **23e** was employed, the diastereoselectivity of the [4 + 2] cycloaddition was considerably lower; thus, with complex **7a** the endo isomer **24e** was formed with 50% de (Table 2, entry 5), whereas with carbene complex **7b** both diastereoisomers **24g** and *rac*-**25g** were formed in equal amounts (Table 2, entry 7). The cycloadducts **24** and *rac*-**25**, which were separated by silica gel column chromatography, displayed both notable physical and spectroscopic differences. Whereas the exo isomers *rac*-**25** are yellow solids, the endo cycloadducts **24** are dark orange solids. On the other hand, in the ^{13}C NMR spectra the carbenic carbon signal of the endo isomers **24** appears at values of δ significantly higher than that of the corresponding exo isomers *rac*-**25** (Table 2). The stereochemistry of endo cycloadducts **24** was ascertained by an X-ray crystallographic study of **24c**.[33] The relative configuration of amino-substituted carbene complex **24f** has been assumed by physical analogy (orange solid) as well as similarity in the carbene carbon ^{13}C NMR chemical shift of this compound with those of the alkoxy-substituted endo cycloadducts **24a**−**e**,**g**.

Finally, we observed that the reaction of bicyclic carbene complex **7g**, which has the C−C double bond inside a fused six-membered ring, with 2-morpholino diene **23a** did not produce the corresponding Diels−Alder adduct, but instead bicyclic diene **26** was isolated (Scheme 6). The structure of this BF_2-chelated amino dienol ether denoted that amino diene **23a** did behave only as a base, promoting the elimination of the pentacarbonylchromium fragment of the vinylcarbene complex **7g**. Similar base-induced transformations of alkoxy-alkylcarbene complexes to enol ethers are well-precedented.[34]

Diels−Alder Reactions of Complexes 7 with Chiral 2-Amino 1,3-Dienes. Given the high selectivity observed in the previous experiments, we decided to investigate the reactions of chelate boroxycarbene complexes **7** with enantiomerically pure 2-amino dienes **27** derived from (*S*)-prolinol *O*-benzyl or *O*-methyl ether. The results of these reactions, which were conducted under above conditions, are indicated in Scheme 7 and Table 3. Surprisingly, we found that treatment of carbene complexes **7a**,**b** with chiral dienes **27a**−**f**, which bear an additional oxygen substituent, afforded exclusively, and in sharp contrast to the results with the structurally similar 2-morpholino dienes **23**, the corresponding exo Diels−Alder adduct **25** with moderate yields but with a high level of enantioselectivity (Table 3, entries 1−7). The use of the *O*-benzyl or *O*-methyl ether derivative of (*S*)-prolinol as the chiral auxiliary group led roughly to the same level of asymmetric induction (Table 2, entries 1 and 4 *versus* 6 and 7, respectively). It is worth noting that these [4 + 2] cycloaddition reactions generate with high enantioselectivity spiranic carbene complexes[35] containing three contiguous stereogenic centers, one of which is a quaternary carbon atom.[36,37] On the other hand, the reaction of carbene complex **7a** with chiral cyclic amino diene **27g**, which does not contain an additional 5-alkoxy group, provided the expected exo cycloadduct **15** but disappointingly with a very low enantiomeric excess (Table 3, entry 8). A single-crystal X-ray structure determination of compound **25a** established the absolute configuration as depicted in Scheme 8 and confirmed the relative configuration of exo cycloadducts **25**.[24]

The observed absolute configuration would correspond in a hypothetical more or less concerted Diels−Alder reaction, taking place with an exo diene−dienophile orientation to dienophile addition to the π-face of the chiral diene, which appears to be the sterically more hindered one (Scheme 8, structure **A**), which suggests that the mechanism of these reactions is unlikely to be a concerted process and that presumably these [4 + 2]

(33) Crystal data for **24c**: $C_{22}H_{28}BCrF_2NO_8{\cdot}CH_2Cl_2$, M_r = 620.19, monoclinic, space group $P2_1/c$, a = 11.914(8) Å, b = 10.86(3) Å, c = 21.52(7) Å, β = 90.8(2)°, V = 2786(12) Å^3, Z = 4, D_x = 1.47 g cm^{-3}, μ = 4.53 cm^{-1}, $F(000)$ = 1280. Final conventional R = 0.047 and wR2 = 0.125 for 3053 "observed" reflections and 451 variables, GOF = 0.941. Red crystal, size 0.26 × 0.26 × 0.16 mm.

(34) (a) Fischer, E. O.; Plabst, D. *Chem. Ber.* **1974**, *107*, 3326. (b) Lattuada, L.; Licandro, E.; Maiorana, S.; Papagni, A. *J. Chem. Soc., Chem. Commun.* **1991**, 437. (c) Barluenga, J.; Montserrat, J. M.; Flórez, J.; García-Granda, S.; Martín, E. *Chem. Eur. J.* **1995**, *1*, 236.

(35) For conventional spirocyclic Fischer carbene complexes, see: (a) Baldoli, C.; Del Buttero, P.; Licandro, E.; Maiorana, S.; Papagni, A.; Zanotti-Gerosa, A. *J. Organomet. Chem.* **1994**, *476*, C27. (b) Dötz, K. H.; Neuss, O.; Nieger, M. *Synlett* **1996**, 995. (c) Schmidt, B.; Kocienski, P.; Reid, G. *Tetrahedron* **1996**, *52*, 1617. See also ref 19f.

(36) For a review regarding the asymmetric creation of quaternary carbon centers, see: Fuji, K. *Chem. Rev.* **1993**, *93*, 2037.

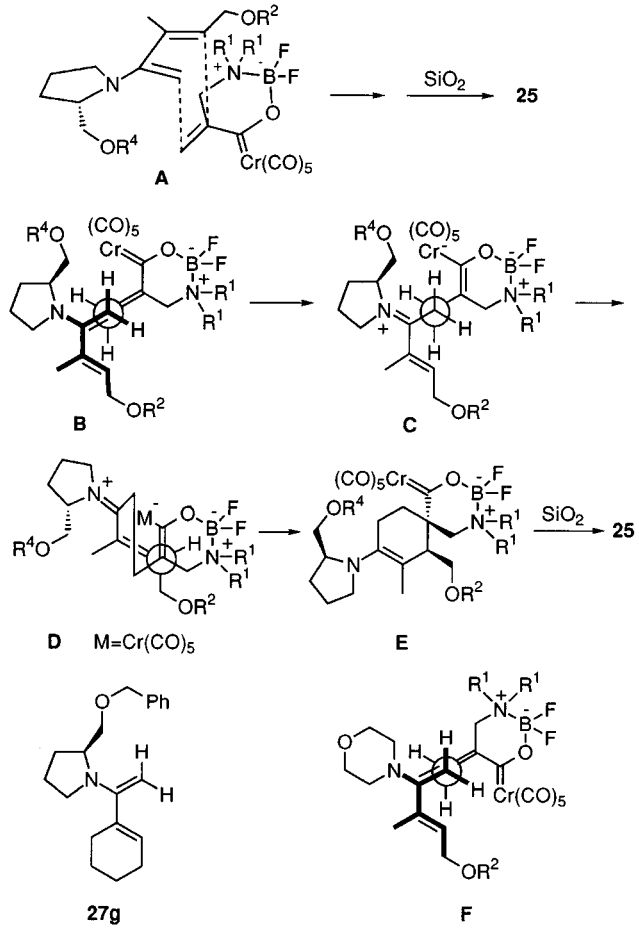
(37) For a recent asymmetric Diels−Alder reaction of a chiral 1-amino-3-siloxy-1,3-butadiene leading to cyclohexenones with a quaternary chiral center, see: Kozmin, S. A.; Rawal, V. H. *J. Am. Chem. Soc.* **1997**, *119*, 7165.

Table 3. Asymmetric Exo-Selective Diels−Alder Reactions of Carbene Complexes **7** with Chiral Amino Dienes **27**

entry	complex **7**	R^1	diene **27**	R^2	R^3	R^4	product	yield[a] (%)	ee[b] (%)
1	**7a**	Et	**27a**	MeO	Me	$PhCH_2$	**25a**	39	92
2	**7a**	Et	**27b**	$PhCH_2O$	Me	$PhCH_2$	**25b**	50	93
3	**7a**	Et	**27c**	$CH_2{=}CHCH_2O$	Me	$PhCH_2$	**25c**	26	76
4	**7a**	Et	**27d**	Me_3SiO	Me	$PhCH_2$	**25e**	44	90
5	**7b**	$PhCH_2$	**27d**	Me_3SiO	Me	$PhCH_2$	**25g**	23	90
6	**7a**	Et	**27e**	MeO	Me	Me	**25a**	43	74
7	**7a**	Et	**27f**	Me_3SiO	Me	Me	**25e**	60	93
8	**7a**	Et	**27g**	$-(CH_2)_3-$		$PhCH_2$	**15**	45	11

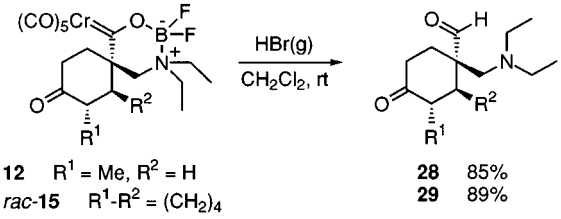
[a] Isolated yield based on the corresponding carbene complex **7**. [b] Enantiomeric excess determined by HPLC analysis on a chiral support (Chiralcel OD-H column) in comparison with the corresponding racemic mixtures.

Scheme 8



cycloadditions take place in a sequential fashion involving zwitterionic species[38] and with the observed diastereoselectivity controlled by electrostatic interactions. Thus, the above results can be rationalized by a stepwise mechanism model (Scheme 8), assuming an initial *anti* nucleophilic attack (Michael-type addition) of the enamine unit to the electrophilic vinylcarbene complex at the sterically least hindered face of the diene.[39] This approach topology **B** could be favored by a greater number of close contacts of the metal center with the prolinol unit than with the vinyl substituent of the enamine. The zwitterionic intermediate **C** thus formed would undergo final ring closure by a subsequent Michael addition of the carbene enolate-type moiety to the resulting α,β-unsaturated iminium salt, which would occur with the CH_2OR^2 unit positioning itself *anti* to the metal fragment **D**. Finally, conversion of the enamine **E** to ketone **25** creates the third contiguous stereogenic center in a highly stereoselective way. The lack of face selectivity observed in the reaction with chiral 2-amino diene **27g**, which could be related to the absence of the vinylic alkoxymethyl substituent and/or the endocyclic nature of the nonenaminic C−C double bond, is, thus far, not well understood. The endo stereoselectivity observed in the reactions with 2-morpholino dienes **23** could be explained likewise by this mechanistic model but assuming the opposite relative topicity shown in **F**. This preference would be a consequence of the absence of the oxygen-containing substituent at C-2 of the amine, and therefore, the greater number of close contacts of the metal center will be with the vinyl alkoxymethyl group.

Scheme 9



Transformation of [4 + 2] Cycloadducts to Metal-Free Organic Products. The formation of metal-free organic products from the spiro BF_2 chelate metal-complexed cycloadducts was carried out by employing known reactions of Fischer carbene complexes. Thus, simultaneous removal of both the pentacarbonylmetal fragment and the BF_2 group was readily achieved by treatment with hydrogen bromide.[40] Bubbling this gas into a dichloromethane solution of racemic carbene complexes **12** and *rac*-**15** furnished the corresponding amino aldehydes **28** and **29**, respectively, as diastereomerically pure compounds (Scheme 9). Unfortunately these strong acid conditions failed with chiral carbene complexes **25a** and **25e**, perhaps due to the acid-sensitive nature of the methoxy or (trimethylsilyl)oxy substituents present in these cycloadducts.

Alternatively, the formation of metal-free organic products was accomplished in a two-step and more general sequence. First the chromium pentacarbonyl fragment was selectively removed by oxidative cleavage either with ceric ammonium nitrate (CAN)[41] or methyl(trifluoromethyl)dioxirane (TFMD).[42]

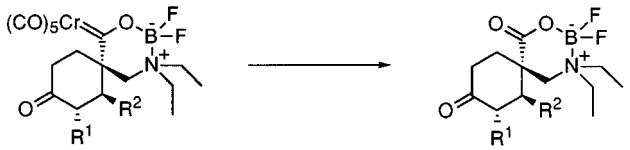
(38) Indeed, when under analogous reaction conditions carbene complex **7a** was treated with the *Z* isomer of diene **27a**, a 2.5:1 mixture of two open-chain diastereomeric keto aldehydes resulting from an initial Michael-type addition of the diene enaminic carbon to the β carbon of the vinylcarbene complex was obtained. These results will be reported separately. See also ref 17f.

(39) For chiral 2-amino 1,3-dienes **27** has been assumed to be of lower energy since the conformation in which the alkoxymethyl side chain of the chiral auxiliary is located as far away as possible from the methyl group at the C-3 position: (a) Enders, D.; Meyer, O.; Raabe, G. *Synthesis* **1992**, 1242. (b) Barluenga, J.; Aznar, F.; Martín, A.; Vázquez, J. T. *J. Am. Chem. Soc.* **1995**, *117*, 9419. (c) Barluenga, J.; Aznar, F.; Ribas, C.; Valdés, C.; Fernández, M.; Cabal, M. P.; Trujillo, J. *Chem. Eur. J.* **1996**, *2*, 805.

(40) See refs 16 and 17b and: Anderson, B. A.; Wulff, W. D.; Rahm, A. *J. Am. Chem. Soc.* **1993**, *115*, 4602.

(41) Casey, C. P.; Boggs, R. A.; Anderson, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 8947 and ref 28a.

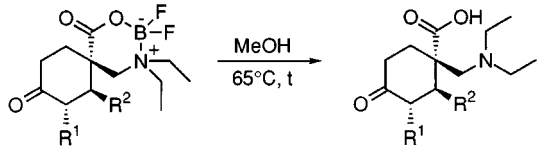
Table 4. Oxidation of Cycloadducts **12**, *rac*-**15**, **18**, and **25a**−**c**



entry	carbene complex	R^1	R^2	oxidation method[a]	product	yield[b] (%)
1	**12**	Me	H	A	**30**	76
2	**12**	Me	H	B	**30**	90
3	**18**		$-(CH_2)_3-$	B	**31**	93
4	*rac*-**15**		$-(CH_2)_4-$	A	**32**	70
5	*rac*-**15**		$-(CH_2)_4-$	B	**32**	90
6	**25a**	Me	$MeOCH_2$	A	**33**	80
7	**25b**	Me	$PhCH_2OCH_2$	A	**34**	73
8	**25c**	Me	$CH_2{=}CHCH_2OCH_2$	A	**35**	88

[a] Method A: CAN, acetone/THF, rt. Method B: TFMD, CH_2Cl_2, 0 °C. [b] Isolated yield based on the corresponding starting carbene complex.

Scheme 10



32 R^1-R^2 = $(CH_2)_4$ t = 3 h **36** 58%
33 R^1 = Me, R^2 = $MeOCH_2$ t = 1 h **37** 50%

Racemic **12**, *rac*-**15**, and **18** or chiral **25a**−**c** carbene complexes could be easily oxidized to the corresponding BF_2-protected β-amino acids **30**−**35** by treatment with either of the above-mentioned oxidants (Table 4).[43] The chemical yields were higher when TFMD was used (Table 4, entries 2 and 5 *vs* 1 and 4, respectively). Finally, the chelate BF_2 complex was cleaved by methanolysis (Scheme 10). Heating racemic BF_2 adduct **32** or the chiral derivative **33** in refluxing methanol for 3 and 1 h, respectively, led to the corresponding α,α-disubstituted β-amino acids **36** and **37** each as a single diastereoisomer. When the methanol solution of boron chelate complex **33** was refluxed for a longer period of time (3 h), epimerization of the stereogenic center α to the ketone carbonyl group took place and β-amino acid **37** was isolated as a 2:1 mixture of diastereoisomers.

In summary, a novel type of group 6 amino-functionalized s-cis vinylcarbene complexes with a cyclic BF_2-chelated structure is described. The Diels−Alder reactions of these nonconventional Fischer carbene complexes with 2-amino 1,3-dienes take place under mild conditions and with high regioselectivity and exo or endo selectivity depending on the substitution pattern of the diene. In addition, the exclusive formation with a high level of asymmetric induction of the generally less accessible exo cycloadduct was observed when chiral 2-amino dienes were employed. The spiro carbene complexes thus synthesized can be easily transformed into β-amino aldehydes or β-amino acids containing an additional carbonyl group.

Experimental Section

General Methods. All reactions involving organometallic species were carried out under an atmosphere of dry N_2 using oven-dried glassware and syringes. TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator. Flash column chromatography was carried out on silica gel 60, 230−240 mesh, or basic aluminum oxide, 70−290 mesh. NMR (^1H, ^{13}C) spectra were recorded on a 200 or a 300 MHz spectrometer with tetramethylsilane (δ = 0.0, ^1H NMR), $CDCl_3$ (δ = 77.0, ^{13}C NMR), or CD_2Cl_2 (δ = 54.2, ^{13}C NMR) as internal standard. ^{19}F NMR spectra were acquired on a 200 MHz spectrometer, and chemical shifts are referenced relative to external CCl_3F. Low-resolution (LRMS) and high-resolution (HRMS) mass spectra were obtained using electron impact (EI) ionization at 70 eV. Suitable single crystals for X-ray structure analysis were obtained by liquid diffusion of hexane into saturated CH_2Cl_2 solutions at −30 °C. Enantiomer compositions were determined by HPLC analysis carried out on a Chiralcel OD-H chiral column with a UV/vis photodiode array detector and employing mixtures of hexane/THF 6−12:1 as eluants; flow rates between 0.8 and 1.0 mL/min; the racemic compounds were used to choose the operating conditions for the resolution of the enantiomer peaks. Optical rotations were measured at the sodium line at ambient temperature (samples concentrations are given in g/100 mL of solvent).

Materials. All commercially available reagents were used without further purification unless otherwise indicated. The solvents were distilled under positive pressure of dry N_2 before use: THF and Et_2O from sodium benzophenone ketyl and hexane and CH_2Cl_2 from P_2O_5. $Et_2O{\cdot}BF_3$ was distilled prior to use. Methyl(trifluoromethyl)dioxirane (TFMD) was prepared following the literature procedure.[42a] The preparation of (2-bromoallyl)amines **6**, using slight modifications of published procedures,[44] is provided in the Supporting Information. The previously known 2-amino 1,3-dienes **10**, **13**, **16**, **17**, **23**, and **27e**,**f** were prepared according to the reported method.[39c,45]

Experimental procedures and spectral data for compounds not described here are presented in the Supporting Information.

General Procedure for the Synthesis of Carbene Complexes 7. To a solution of the corresponding amine **6** (25 mmol) in Et_2O (50 mL) was added *t*-BuLi (1.7 M in pentane, 50 mmol) at −60 °C under nitrogen. The mixture was stirred for 2 h at −60 °C and 1 h at room temperature. The resulting solution was added dropwise to a suspension of the appropriate group 6 metal hexacarbonyl (25 mmol) in Et_2O (50 mL) at room temperature. After 1 h, an excess of $Et_2O{\cdot}BF_3$ (3−4 equiv) was added at room temperature and the solution stirred for another 1 h. To the reaction mixture was added silica gel (ca. 15 g), the solvent was removed under reduced pressure, and the residue was transferred to the top of a silica gel column and purified by flash chromatography with mixtures of hexane/CH_2Cl_2 to give compounds **7** as dark red solids. Yields are reported in Table 1.

Pentacarbonyl(4,4-diethyl-3,3-difluoro-6-methylene-2-oxa-4-aza-3-boracyclohexylidene)chromium (7a): red solid; R_f 0.25 (hexane/

(42) (a) Mello, R.; Fiorentino, M.; Sciacovelli, O.; Curci, R. *J. Org. Chem.* **1988**, *53*, 3890. (b) Lluch, A. M.; Jordi, L.; Sánchez-Baeza, F.; Ricart, S.; Camps, F.; Messeguer, A.; Moretó, J. M. *Tetrahedron Lett.* **1992**, *33*, 3021. (c) Ferrer, M.; Sánchez-Baeza, F.; Messeguer, A.; Diez, A.; Rubiralta, M. *J. Chem. Soc., Chem. Commun.* **1995**, 293.

(43) For recent references of amino acid−metal complexes, see: (a) Vedejs, E.; Fields, S. C.; Schrimpf, M. R. *J. Am. Chem. Soc.* **1993**, *115*, 11612. (b) Grotjahn, D. B.; Groy, T. L. *J. Am. Chem. Soc.* **1994**, *116*, 6969.

(44) (a) Pollard, C. B.; Parcell, R. F. *J. Am. Chem. Soc.* **1951**, *73*, 2925. (b) Ficini, J.; Sarrade-Loucheur, G.; Normant, H. *Bull. Soc. Chim. Fr.* **1962**, 1219. (c) Mori, M.; Chiba, K.; Okita, M.; Kayo, I.; Ban, Y. *Tetrahedron* **1985**, *41*, 375.

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CH_2Cl_2 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.2 (t, J = 7.3 Hz, 6H), 2.65 (m, 2H), 3.15 (m, 2H), 3.50 (s, 2H), 6.25 (m, 1H), 6.73 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 7.4, 45.9, 54.8, 140.2, 144.6, 217.3, 225.3, 339.6; ^{19}F NMR (188.15 MHz, $CDCl_3$) δ −153.9 (m); IR (KBr) ν 2060, 1919, 1628 cm^{-1}; LRMS (70 eV, EI) m/z 381 (M^+, 2), 241 (90), 86 (100), 52 (78). Anal. Calcd for $C_{13}H_{14}BCrF_2NO_6$: C, 40.97; H, 3.70; N, 3.67. Found: C, 41.81; H, 3.76; N, 3.67.

Pentacarbonyl(4-ethyl-3,3-difluoro-6-methylene-4-phenyl-2-oxa-4-aza-3-boracyclohexylidene)chromium (7c): red solid; R_f 0.32 (hexane/CH_2Cl_2 1:1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.85 (t, J = 7 Hz, 3H), 3.15 (m, 1H), 3.65 (m, 1H), 4.10 (AB q, J = 14.6 Hz, $\Delta\nu$ = 20.7 Hz, 2H), 6.22 (s, 1H), 6.65 (s, 1H), 7.4 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 7.4, 53.2, 54.7, 122.5, 128.9, 129.9, 139.7, 139.9, 145.5, 217.1, 225.3, 339.5; ^{19}F NMR (188.15 MHz, $CDCl_3$) δ −151.8 (m); IR (KBr) υ 2062, 1936 cm^{-1}; LRMS (FAB) m/z 429 (M^+, 7), 289 (80), 106 (100), 52 (46). Anal. Calcd for $C_{17}H_{14}BCrF_2NO_6$: C, 47.58; H, 3.28; N, 3.26. Found: C, 47.26; H, 3.45; N, 3.47.

Pentacarbonyl[2-[(*N*,*N*-dibenzylamino)methyl]-1-hydroxy-2-propenylidene]chromium (Betaine) (9). To a solution of amine **6b** (1.58 g, 5 mmol) in Et_2O (20 mL) was added *t*-BuLi (1.7 M in pentane, 10 mmol) at −80 °C under nitrogen. The mixture was stirred for 2 h at −80 °C and 1 h at room temperature. The resulting solution was added dropwise to a suspension of $Cr(CO)_6$ (1.10 g, 5 mmol) in Et_2O (20 mL) at room temperature. After the solution was stirred for 2 h, silica gel (ca. 3 g) was added to the reaction mixture, the solvent was removed under reduced pressure, and the residue was transferred to the top of a silica gel column and purified by flash chromatography (hexane/CH_2Cl_2 1:1) to give compound **9** as an orange solid (1.48 g, 65% yield): R_f 0.23 (hexane/CH_2Cl_2 1:1); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 3.6 (s, 2H), 4.0 (s, 4H), 5.9 (s, 1H), 6.4 (s, 1H), 7.3−7.6 (m, 10H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 56.6, 57.4, 129.8, 130.4, 130.7, 130.9, 132.6, 146.4, 221.1, 226.7, 319.8; IR (THF) ν 2042, 1965 cm^{-1}; LRMS (FAB) m/z 429 (M^+ − 28, 70), 91 (100).

General Procedure for the Diels−Alder Cycloadditions. To a solution of the appropriate carbene complex **7** (2 mmol) in THF (20 mL) was added dropwise a solution of the corresponding 2-amino 1,3-diene **10**, **13**, **16**, **17**, **23**, or **27** (2 mmol) in THF (10 mL) at −78 °C under nitrogen. The reaction mixture was allowed to slowly warm to room temperature overnight. Then silica gel (ca. 5 g) was added, the solvent was removed, and the residue was transferred to the top of a silica gel column and purified by flash chromatography (hexane/CH_2Cl_2) to give the corresponding Diels−Alder cycloadducts. The chromatographic purification of cycloadducts **14** and **20a** was performed on basic aluminum oxide. Yields are listed in Schemes 3−7 and Tables 2 and 3.

Pentacarbonyl[4,4-diethyl-3,3-difluoro-8-methyl-9-(*N*-methyl-*N*-phenylamino)-2-oxa-4-aza-3-boraspiro[5.5]undec-8-en-1-ylidene]chromium (11): yellow solid; R_f 0.20 (hexane/Et_2O/CH_2Cl_2 5:1:1); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.30 (m, 6H), 1.65−1.75 (m with s at 1.69, 4H), 1.95−2.15 (m, 2H), 2.30 (m, 1H), 2.6−3.3 (m with s at 3.0, 10H), 3.6 (m, 1H), 6.57 (d, J = 7.9 Hz, 2H), 6.75 (t, J = 7 Hz, 1H), 7.23 (t, J = 8 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 7.3, 7.8, 18.2, 21.2, 33.6, 36.6, 41.6, 46.6, 47.8, 57.8, 57.8, 111.8, 116.6, 127.4, 129.2, 135.7, 147.1, 216.9, 223.7, 364.0; IR (KBr) ν 2058, 1931, 1599 cm^{-1}; LRMS (FAB) m/z 554 (M^+, 10), 470 (73), 414 (84).

(6*S,1′*S**)-Spiro[pentacarbonyl(4,4-diethyl-3,3-difluoro-2-oxa-4-aza-3-boracyclohexylidene)chromium-6,2′-5′-(*N*-methyl-*N*-phenylamino)bicyclo[4.4.0]-5′-decene] (14):** yellow solid; R_f 0.25 (Al_2O_3, hexane/Et_2O/CH_2Cl_2 8:1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.1−1.5 (m, 9H), 1.6−1.95 (m, 4H), 2.1−2.25 (m, 1H), 2.3−2.55 (m, 2H), 2.65−3.35 (m with s at 3.02, 11H), 3.55 (d, J = 11.2 Hz, 1H), 6.60 (d, J = 7.5 Hz, 2H), 6.76 (t, J = 7 Hz, 1H), 7.26 (t, J = 7.3 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 6.4, 8.3, 22.0, 24.6, 24.7, 26.8, 27.4, 33.0, 36.5, 43.8, 45.3, 49.6, 50.8, 61.1, 111.7, 116.4, 129.1, 133.5, 133.7, 147.1, 216.9, 223.5, 365.8; ^{19}F NMR (188.15 MHz, $CDCl_3$) δ −152.8 (m), −155.2 (m); IR (KBr) ν 2056, 1931 cm^{-1}. Anal. Calcd for $C_{28}H_{33}BCrF_2N_2O_6$: C, 56.58; H, 5.59; N, 4.71. Found: C, 56.28; H, 5.61; N, 5.28.

(6*S,7*R**,8*S**)-[7-(Allyloxymethyl)-4,4-diethyl-3,3-difluoro-8-methyl-9-oxo-2-oxa-4-aza-3-boraspiro[5.5]-1-undecylidene]pentacarbonylchromium (24c):** orange solid; R_f 0.35 (CH_2Cl_2); ^{1}H NMR (200 MHz, CD_2Cl_2) δ 1.01 (d, J = 5.4 Hz, 3H), 1.25 (m, 6H), 2.2−3.4 (m, 12H), 3.65 (m, 2H), 4.0 (m, 2H), 5.15 (m, 2H), 5.8 (m, 1H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 8.2, 9.4, 12.0, 37.7, 37.9, 43.2, 49.1, 51.7, 52.1, 60.9, 62.0, 66.2, 73.3, 117.5, 134.7, 208.0, 217.4, 225.1, 381.3; ^{19}F NMR (188.15 MHz, $CDCl_3$) δ −146.2 to −147.8) (m); IR (KBr) ν 2060, 1935, 1707 cm^{-1}. Anal. Calcd for $C_{22}H_{28}BCrF_2NO_8$: C, 49.37; H, 5.27; N, 2.62. Found: C, 49.15; H, 5.21; N, 2.59.

(6*S*,7*S*,8*S*)-Pentacarbonyl[4,4-diethyl-3,3-difluoro-7-(methoxymethyl)-8-methyl-9-oxo-2-oxa-4-aza-3-boraspiro[5.5]-1-undecylidene]chromium (25a): yellow solid; $[\alpha]^{20}_D$ = −4.5 (*c* 0.70, $CHCl_3$); R_f 0.18 (hexane/CH_2Cl_2 1:2); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.1 (m, 6H), 1.32 (t, J = 7 Hz, 3H), 1.85 (m, 1H), 2.35−2.6 (m, 3H), 2.6−2.85 (m, 3H), 3.05−3.4 (m with s at 3.23, 9H), 4.15 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 6.1, 8.8, 11.5, 35.6, 36.5, 42.2, 43.0, 50.4, 50.7, 51.7, 58.4, 61.6, 69.5, 208.9, 216.7, 223.0, 365.2; IR (KBr) ν 2062, 1981, 1942, 1929, 1709 cm^{-1}. Anal. Calcd for $C_{20}H_{26}BCrF_2NO_8$: C, 47.17; H, 5.15; N, 2.75. Found: C, 46.86; H, 5.10; N, 2.72.

(6*S*,7*S*,8*S*)-[7-[(Allyloxy)methyl]-4,4-diethyl-3,3-difluoro-8-methyl-9-oxo-2-oxa-4-aza-3-boraspiro[5.5]-1-undecylidene]pentacarbonylchromium (25c): yellow solid; $[\alpha]^{20}_D$ = 4.8 (*c* 0.24, $CHCl_3$); R_f 0.23 (hexane/CH_2Cl_2 1:2); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.15 (m, 6H), 1.33 (t, J = 6.7 Hz, 3H), 1.9 (m, 1H), 2.45 (m, 2H), 2.6 (m, 1H), 2.65−2.9 (m, 3H), 3.1 (m, 3H), 3.3 (m, 2H), 3.51 (dd, J = 10.9, 5.2 Hz, 1H), 3.78 (dd of AB q, J = 12.3, 5.8 Hz, 1H), 3.98 (dd of AB q, J = 12.3, 5.6 Hz, 1H), 4.27 (d, J = 13.9 Hz, 1H), 5.2 (m, 2H), 5.85 (m, 1H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 6.7, 9.4, 12.1, 36.5, 37.3, 43.0, 44.1, 51.3, 51.4, 52.7, 62.6, 68.2, 72.6, 117.4, 135.0, 209.7, 217.6, 224.1, 366.4; ^{19}F NMR (188.15 MHz, CD_2Cl_2) δ −153.0 (m), −156.2 (m); IR (KBr) ν 2060, 1981, 1933, 1715 cm^{-1}.

Acid Hydrolysis of Carbene Complexes 11, 14, 19, and 21a,a′. To a solution of the corresponding carbene complex (1 mmol) in THF (20 mL) was added a solution of 3 N HCl (10 mL) at room temperature. The reaction mixture was stirred during 3 h and then was extracted with CH_2Cl_2. The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo, and the residue was purified by flash column chromatography (hexane/CH_2Cl_2) on silica gel. Yields are listed in Schemes 3 and 4. This method was used to prepare compounds **12**, *rac*-**15**, and **22**.

(6*S,8*S**)-Pentacarbonyl(4,4-diethyl-3,3-difluoro-8-methyl-9-oxo-2-oxa-4-aza-3-boraspiro[5.5]-1-undecylidene)chromium (12):** yellow solid; R_f 0.19 (hexane/CH_2Cl_2 1:2); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.0−1.5 (m, 9H), 1.95 (m, 2H), 2.35−2.95 (m, 6H), 2.95−3.30 (m, 5H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 8.2, 8.4, 14.8, 37.7, 38.4, 41.0, 46.4, 47.9, 48.7, 58.3, 59.5, 209.2, 217.7, 224.4, 364.0; ^{19}F NMR (188.15 MHz, CD_2Cl_2) δ −153.7 (s); IR (KBr) ν 2060, 1934, 1715 cm^{-1}; LRMS (FAB) m/z 465 (M^+, 14), 353 (69), 325 (100). Anal. Calcd for $C_{18}H_{22}BCrF_2NO_7$: C, 46.48; H, 4.77; N, 3.01. Found: C, 46.13; H, 4.85; N, 2.90.

(4*S,6*S**,1′*S*,*6′*S**)-Spiro[pentacarbonyl(4-ethyl-3,3-difluoro-4-phenyl-2-oxa-4-aza-3-boracyclohexylidene)chromium-6,2′-bicyclo[4.4.0]decan-5′-one] (22):** yellow solid; R_f 0.24 (hexane/CH_2Cl_2 1:2); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 0.15 (m, 1H), 0.9−1.13 (m, 8H), 1.5−1.8 (m, 3H), 1.9−2.2 (m, 2H), 2.4−2.6 (m, 2H), 3.2−3.85 (m, 5H), 7.4 (m, 5H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 10.5, 25.7, 25.9, 27.1, 28.8, 34.9, 36.9, 49.3, 52.3, 58.6, 59.8, 62.8, 124.4, 130.8, 131.3, 140.1, 208.7, 217.4, 224.0, 368.6; ^{19}F NMR (188.15 MHz, $CDCl_3$) δ −144.7 (m), −147.5 (m); IR (KBr) ν 2062, 1921, 1701 cm^{-1}.

Reaction of Complexes 12 and *rac*-15 with HBr. Preparation of Aldehydes 28 and 29. HBr gas was bubbled into a solution of the corresponding carbene complex **12** or *rac*-**15** (1 mmol) in CH_2Cl_2 (30 mL) at room temperature and under N_2 until the complete disappearance of the starting complex was observed (the reaction was followed by TLC). The reaction mixture was treated with 3 N KOH and then was extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo, and the residue was purified by flash column chromatography (CH_2Cl_2/THF) on silica gel. Yields are reported in Scheme 9.

(1*S,2*S**,6*S**)-2-[(*N*,*N*-Diethylamino)methyl]-5-oxobicyclo[4.4.0]decane-2-carbaldehyde (29):** colorless oil; R_f 0.40 (CH_2Cl_2/THF 1:50); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.98 (t, J = 7 Hz, 6H), 1.1−1.4 (m, 4H), 1.6−1.9 (m, 6H), 2.0−2.6 (m, 8H), 2.85 (d of AB q, J = 14 Hz,

1H), 3.08 (d of AB q, $J = 14$ Hz, 1H), 9.6 (s, 1H); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ 11.1, 24.9, 25.7 (2C), 27.1, 28.5, 37.0, 47.2, 48.1, 48.9, 49.5, 51.5, 206.6, 211.1; IR (neat) ν 1712, 1720 cm^{-1}; HRMS (70 eV, EI) calcd for $C_{16}H_{27}NO_2$ (M^+) 265.2041, found 265.2042.

Oxidation of Complexes 12, *rac*-15, and 25a−c. Method A. To a solution of the corresponding carbene complex (1 mmol) in THF (20 mL) was added a solution of ceric ammonium nitrate (CAN, 1.5 mmol) in acetone (20 mL) at room temperature. The reaction mixture was stirred for 15 min, and then solvents were removed under reduced pressure. The resultant crude material was extracted with CH_2Cl_2. After filtration of insoluble solids, the resulting solution was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel. This method was used to prepare compounds **30** and **32**−**35**. Yields are listed in Table 4.

(6*S*,7*S*,8*S*)-4,4-Diethyl-3,3-difluoro-7-(methoxymethyl)-8-methyl-2-oxa-4-aza-3-boraspiro[5.5]undecane-1,9-dione (33): white solid; $[\alpha]^{20}_D = +3.09$ (*c* 1.32, $CHCl_3$); R_f 0.45 (CH_2Cl_2); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.02 (d, $J = 6.4$ Hz, 3H), 1.19 (t, $J = 7.3$ Hz, 3H), 1.28 (t, $J = 7.3$ Hz, 3H), 2.2 (m, 3H), 2.45 (m, 3H), 2.9 (m, 2H), 3.2 (m, 2H), 3.25 (s, 3H), 3.35 (s, 1H), 3.45 (d, $J = 3.1$ Hz, 2H), 4.15 (d, $J = 13.9$ Hz, 1H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 7.2, 9.2, 11.5, 36.1, 36.9, 42.5, 45.5, 47.5, 50.3, 51.6, 52.1, 59.0, 71.3, 173.1, 210.0; ^{19}F NMR (188.15 MHz, CD_2Cl_2) δ −151.2 (m), −153.6 (m); IR (KBr) ν 1711 cm^{-1}.

Oxidation of Complexes 12, 18, and *rac*-15. Method B. To a stirred solution of the corresponding carbene complex (1 mmol) in CH_2Cl_2 (20 mL) was added at 0 °C a 0.6 M solution of methyl(trifluoromethyl)dioxirane (TFMD) in 0.5 mmol fractions every 30 min until the complete disappearance of the starting complex was observed (ca. 4 mmol of TFMD was needed, TLC monitoring). The solid residue was eliminated by filtration, and the filtrate solution was concentrated under vacuum. The resulting residue was purified by flash column chromatography on silica gel. This method was used to prepare compounds **30**−**32**. Yields are listed in Table 4.

(6*S,1′*S**,6′*S**)-Spiro[4,4-diethyl-3,3-difluoro-2-oxa-4-aza-3-bora-1-cyclohexanone-6,2′-bicyclo[4.4.0]decan-5′-one] (32):** white solid; R_f 0.46 (CH_2Cl_2/EtOAc 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.1−1.4 (m with 2t at 1.24 and 1.34, $J = 7$ Hz, 8H), 1.8 (m, 4H), 2.1 (m, 3H), 2.45 (m, 3H), 2.9 (m, 3H), 3.22 (s, 2H), 3.4 (m, 3H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 7.4, 9.2, 25.5, 25.9, 26.4, 28.7, 35.9, 36.9, 45.3, 46.5, 48.4, 50.2, 51.5, 51.6, 172.4, 208.8; ^{19}F NMR (188.15 MHz, CD_2Cl_2) δ −151.4 (m), −152.4 (m); IR (KBr) ν 1711, 1721 cm^{-1}. Anal. Calcd for $C_{16}H_{26}BF_2NO_3$: C, 58.38; H, 7.96; N, 4.25. Found: C, 58.02; H, 8.12; N, 4.33.

Reaction of BF_2-Protected Amino Acids 32 and 33 with Methanol. Obtention of Amino Acids 36 and 37. A solution of the corresponding BF_2-protected amino acid (0.5 mmol) in MeOH (20 mL) was heated at reflux (during 3 h for **32** and 1 h for **33**). The reaction mixture was concentrated in vacuo, and the resulting residue was purified by flash column chromatography on silica gel. Yields are listed in Scheme 10.

(1*S*,2*S*,3*S*)-1-[(*N*,*N*-Diethylamino)methyl]-2-(methoxymethyl)-3-methyl-4-oxocyclohexanecarboxylic acid (37): white solid; R_f 0.46 (CH_2Cl_2/CH_3OH 10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (d, $J = 5.8$ Hz, 3H), 1.25 (t, $J = 7.2$ Hz, 6H), 2.15 (m, 3H), 2.45 (m, 3H), 2.9 (m, 2H), 3.05 (m, 2H), 3.15 (d of AB q, $J = 14.6$ Hz, 1H), 3.26 (s, 3H), 3.46 (dd of AB q, $J = 10.93$, 4.3 Hz, 1H), 3.57 (d of AB q, $J = 10.93$ Hz, 1H), 3.66 (d of AB q, $J = 14.6$ Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 10.5, 12.2, 34.6, 36.9, 42.4, 47.9, 48.9, 49.9, 52.1, 59.3, 72.5, 178.9, 211.1; HRMS (70 eV, IE) calcd for $C_{15}H_{27}NO_4$ (M^+) 285.1940, found 285.1953.

X-ray Structure Determinations. Data were collected on a Nonius CAD-4 single-crystal diffractometer, Mo Kα radiation (graphite crystal monochromator, $\lambda = 0.710\,73$ Å), $T = 200(2)$ K (Oxford CRYOSTREAM).[46] The structures were solved by Patterson methods using the program DIRDIF.[47] Refinement on F^2, using SHELXL93.[48] The maximum shift to esd ratio in the last full-matrix least-squares cycle was less than 0.001 for all structures. The CH_2Cl_2 solvent molecule, present in the packing of all structures reported, was affected by strong structural disorder resolved in two alternative positions with occupation factors close to 50%. The final difference Fourier map showed no peaks higher than 1.0 eÅ^{-3}. All calculations were made at the University of Oviedo on the Scientific Computer Center and X-ray Group DEC/AXP computers.

Acknowledgment. Support for this research by the Dirección General de Investigación Científica y Técnica (DGICYT) (Grant Nos. PB92-1005 and PB93-0330) is gratefully acknowledged. R.M.C. and A.G.R. thank the Ministerio de Educación y Ciencia for a predoctoral fellowship. The authors thank Prof. A. Messeguer, Dr. F. Sánchez-Baeza, and Dra. A. M. Lluch for performing the initial oxidation experiments with TFMD and Dr. P. Bernad for expert assistance in mass spectral analysis.

Supporting Information Available: Experimental procedures and analytical and spectral data for (*E*)-3-methyl-6-phenyl-6-aza-3-hepten-1-yne, (*S*)-(+)-2-(benzyloxymethyl)pyrrolidine, 2-bromoallylamines **6**, 2-amino dienes **23f** and **27a**−**d**,**g**, and carbene complex **8c**. Analytical and spectral data for compounds **7b**,**d**−**i**, **15**, **18**, **19**, **20a**, **21b**, **24a**,**b**,**d**−**g**, **25b**,**e**,**g**, **26**, **28**, **30**, **31**, and **34**−**36**. Crystallographic experimental sections and tables of X-ray crystal data, final fractional coordinates, thermal parameters, bond lengths and angles, and a crystallographic plot for **9**, **22**, and **24c** (51 pages). See any current masthead page for ordering and Web access instructions. The authors have deposited the atomic coordinates for the three X-ray structures with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

JA972588O

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