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High diastereoselective Michael and aldol additions of Fischer-type alkyl(hydrazino)carbene complexes: synthesis of new hydrazides

Emanuela Licandro [a,*], Dario Perdicchia [a], Stefano Maiorana [a], Clara Baldoli [a], Clelia Giannini [a], Claudia Graiff [b], Antonio Tiripicchio [b]

[a] *Dipartimento di Chimica Organica e Industriale, CNR-Istituto di Scienze e Tecnologie Molecolari and Centro di Eccellenza CISI, Università degli Studi di Milano, Via C. Golgi, 19, I-20133 Milan, Italy*
[b] *Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Parco Area delle Scienze 17/A, I-43100 Parma, Italy*

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Dedicated with admiration to Professor Ernst Otto Fischer on the occasion of his 85th birthday

Abstract

The addition of the enolate, generated from the tetracarbonylethyl(hydrazino)carbene chromium complex **6**, to achiral enones and aldehydes gave the corresponding Michael and aldol adducts in very high chemical yield and d.e.. Some of the new δ-keto and β-hydroxy hydrazino carbene complexes have been oxidised to give the corresponding hydrazides in high yield. A spectroscopic study to establish the geometry of the enolate generated from **6** has also been performed.

Keywords: Fischer-type hydrazinocarbenes; Hydrazides; Stereoselective Michael addition; Stereoselective aldol addition; Oxidation of Fischer complexes

1. Introduction

Fischer carbene complexes **1** (Scheme 1) are a versatile class of organometallic intermediates that have been extensively used as useful stoichiometric reagents in organic synthesis [1]. Much of the considerable current interest concerns the application of such complexes to stereoselective carbon–carbon bond formation because of their particular steric and electronic characteristics, and easy conversion into a very large number of different organic compounds. Moreover, alkylcarbene complexes readily undergo α-deprotonation to give enolate-type carbene complex anions, which have been exploited in a number of stereoselective reactions. They can be subsequently transformed into organic compounds in various ways, the easiest of which is oxidation, which converts the carbon–metal double bond into the C=O bond (Scheme 1).

Most of the published examples of stereoselective reactions involving chromium carbene complexes concern the case in which $R^2 = H$, and include highly stereoselective Michael additions to nitroalkenes [2], enones [3] and aldol reactions [4]. When $R^2 =$ alkyl, the stereoselections depend on the nature of X in the complex: alkoxy carbenes (X = O) have shown variable, but in many cases high stereoselectivity in aldol reactions [5], Michael additions [6] and alkylations with alkyl halides [6c,7]. On the contrary, in the case of amino carbenes (X = N), there are only two references in the literature: one concerning alkylation [8] (but the d.e. products and related configuration are not indicated) and the other the aldol reaction [9] (in which the aldol addition product was obtained in poor yield and without any diastereoselection).

* Corresponding author. Tel.: +39-02-503-14143; fax: +39-02-503-14139.
E-mail address: emanuela.licandro@unimi.it (E. Licandro).

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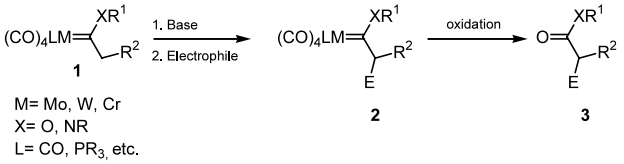
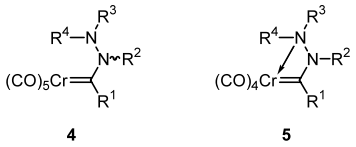


Scheme 1.



Scheme 2.

The differences between the alkoxy and amino complexes are mainly due to the low reactivity of α-substituted amino carbene anions towards electrophiles [10] and unfavourable steric effects.

Over the last few years, we have studied a new class of Fischer-type carbene complexes: the pentacarbonyl alkyl(hydrazino)carbene (**4**) and the tetracarbonyl alkyl(hydrazino)carbene (**5**) (Scheme 2).

In addition to setting up two complementary methods of synthesis [11], we have exploited these new complexes in the formation of a new carbon–carbon bond by means of the generation of the anion in the α-position and reactions with alkyl halides, aldehydes and epoxides [12]. These preliminary studies clearly showed that especially tetracarbonyl hydrazinocarbene complexes **5** have considerable synthetic potential in carbon–carbon bond-forming reactions. In particular, as a result of decreased conformational freedom and easier accessibility to the α-carbon atom in chelate complexes **5** (Scheme 2), it was possible to introduce two different alkyl groups in high-yield, in this position, thus generating a new stereogenic centre [12]. Furthermore, the rigid structure of tetracarbonyl hydrazinocarbene complexes may be useful for achieving a high degree of stereoselective control and then easily converted into the corresponding hydrazides by means of oxidation [13]. One of the main purposes of this research was to study diastereofacial selectivity in Michael and aldol additions of the α-anion of hydrazinocarbene complex **6**. We also succeeded in transforming the products into the corresponding hydrazides by means of oxidation of the functionalised complexes.

2. Results and discussion

2.1. Michael addition

Complex **6**, prepared as previously described by us [12], was transformed into the corresponding anion by means of deprotonation in dry THF at −78 °C using *n*-

Table 1

Entry	Enones	Michael adducts[a]	reaction conditions	d.e. (%)[b]	yields (%)	d.e. (%)[c]
1	**7a**	**8a-9a**	- 78 °C	42	87	47
2	**7b**	**8b-9b**	- 78 °C	92	82	87
			- 30 °C	75	52	70
			- 78 °C 2 eq DMPU	76	86	83
			- 78 °C 4 eq DMPU	22	73	27
3	**7c**	**8c-9c**	- 78 °C	98	60	>98
			- 78 °C 4 eq DMPU	89	59	90
			- 30 °C 4 eq DMPU	90	62	88
			- 78 °C DMPU as cosolvent	74	25	75
4	**7d**	**9d**	- 78 °C	>98	87	>98

[a]Structures of the major products (**9a**–**9d**) are shown. [b]d.e. of the crude reaction products (from ^{1}H-NMR). [c]d.e. after purification by column chromatography (from weights of separated diastereoisomers in entries 2–4 and from the unseparated mixture in entry 1).

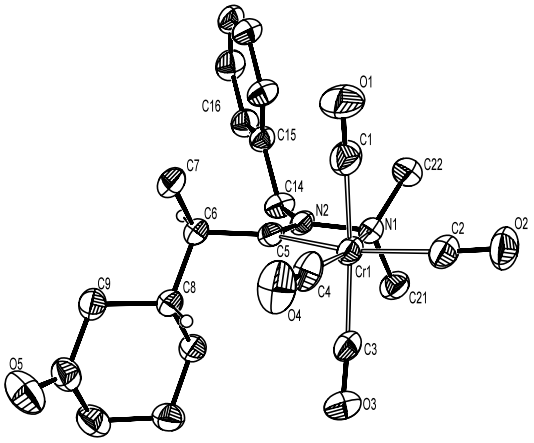
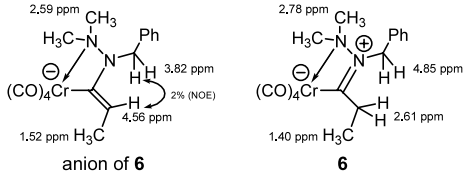


Fig. 1. View of the molecular structure of **9b** together with the atomic numbering system. Thermal ellipsoids are drawn at 30% probability level.

BuLi, and then allowed to react with enones **7a**–**7d** at the same temperature (Scheme 4). The reactions were quenched with saturated NH_4Cl after 3 h, and the products were the diastereoisomeric ketocomplexes **8a**–**8c** and **9a**–**9d** (Scheme 4). The results of these additions are summarised in Table 1. The d.e. were determined by ^{1}H-NMR of the crude products and, with the exception of the reaction with the cyclopentenone (Table 1, entry 1), were very high; in the case of enone **7d**, diastereoselectivity was complete (Table 1, entry 4).

The two diastereoisomers **8** and **9** can be easily separated using column chromatography on silica gel (we were unable to separate the two diastereoisomers in the case of **8a** and **9a** despite we have tried several eluents) and isolated as very stable compounds; the yields were high (except in the case of entry 3) and the d.e. changed little (in favour of the major diastereoisomer) after chromatographic purification. In order to obtain a larger amount of the minor diastereoisomers (**8b** and **8c**) for analytical purposes (and to study the effect of some variables on the reaction products), we changed some reaction parameters such as the temperature (−30 °C) or adding 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) which can split the lithium cation from the anion of complex **6** (see Section 4 for more details). In addition to 2-cyclohexen-1-one (**7b**; Table 1, entry 2) and with the reaction running at −30 °C, d.e. decreased to 75%, and the same reaction run at −78 °C with two and four equivalents of DMPU gave d.e. values of, respectively, 76 and 22%. These two experiments show that the coordination of lithium ion can play an important role in diastereoselectivity. In the reaction with *trans*-1,3-diphenyl-propenone (**7c**; Table 1, entry 3), stereoselectivity was less influenced by the temperature, and it was necessary to use DMPU as a co-solvent in order to decrease the d.e.. However, in this last case, the chemical yield was very low (25%) and about half of the starting complex **6** was recovered from the reaction mixture. The relative configurations of the two stereocentres in complexes **9b** and **9c** were determined by X-ray diffraction methods. Using the spectroscopic data of **9b**, the stereochemistry of the complexes of entries 1 and 4 (Table 1) was assigned on the basis of their ^{13}C-NMR, and showed the characteristic difference in the chemical shift of the CrCCH*C*H$_3$ in the two diastereoisomers. A similar shift has been reported for diastereoisomeric amides [18].

Views of the molecular structures of complexes **9b** and **9c** are given in Figs. 1 and 2, respectively.



Scheme 3. ^{1}H-NMR in THF-D$_8$.

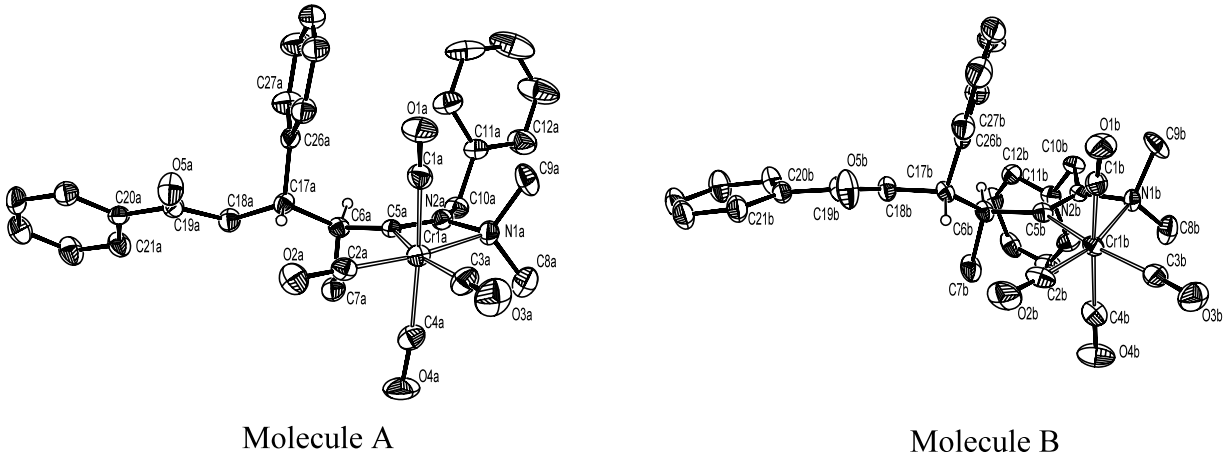
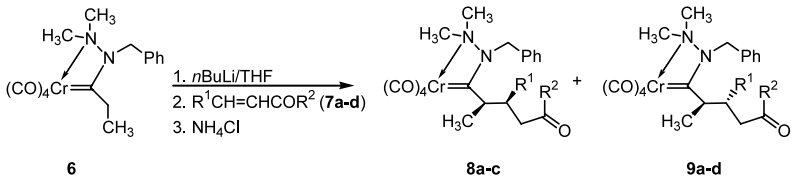


Fig. 2. View of the molecular structure of molecule A and molecule B of complex **9c** together with the atomic numbering system. Thermal ellipsoids are drawn at 30% probability level.



Scheme 4. Michael addition of carbene **6** to enones **7a**–**7d**.

Table 2
Selected bond lengths (Å) and angles (°) for **9b**

Bond distances	
C(5)–Cr(1)	2.031(4)
N(1)–Cr(1)	2.208(4)
N(1)–N(2)	1.458(5)
C(5)–N(2)	1.309(6)
C(5)–C(6)	1.507(6)
C(14)–N(2)	1.474(6)
Bond angles	
N(2)–C(5)–C(6)	120.0(4)
N(2)–C(5)–Cr(1)	101.0(3)
C(6)–C(5)–Cr(1)	139.0(3)
C(5)–C(6)–C(7)	108.4(4)
N(2)–C(14)–C(15)	114.8(4)
N(2)–N(1)–Cr(1)	88.6(2)
C(5)–N(2)–N(1)	107.1(3)
C(5)–Cr(1)–N(1)	63.23(16)

Table 3
Selected bond lengths (Å) and angles (°) for **9c** molecules A and B (in parentheses)

Bond distances	
Cr(1)–N(1)	2.208(5) (2.216(5))
Cr(1)–C(5)	2.044(5) (2.043(6))
N(1)–N(2)	1.463(6) (1.461(5))
N(2)–C(5)	1.324(6) (1.310(6))
N(2)–C(10)	1.500(7) (1.488(6))
O(5)–C(19)	1.223(6) (1.232(6))
C(5)–C(6)	1.507(7) (1.502(7))
C(6)–C(7)	1.552(7) (1.537(7))
C(10)–C(11)	1.509(7) (1.511(7))
Bond angles	
C(5)–Cr(1)–N(1)	63.7(2) (62.9(2))
N(2)–N(1)–Cr(1)	88.9(3) (88.9(3))
C(5)–N(2)–N(1)	107.4(4) (106.9(4))
N(2)–C(5)–C(6)	118.3(5) (118.5(5))
N(2)–C(5)–Cr(1)	100.1(3) (101.1(4))
C(6)–C(5)–Cr(1)	140.5(4) (140.0(4))
N(2)–C(10)–C(11)	114.1(4) (115.6(4))

In the crystals of **9c**, two crystallographically independent complexes (conformers) are present (molecules A and B, respectively), differing for the disposition of the benzyl group with respect to the phenyl ring (on the same side, molecule A, on opposite side, molecule B, Fig. 2). Being the structures of **9b** and **9c** centrosymmetrical, both enantiomers are present in the crystals, with the stereogenic centres C6 and C8 in **9b** and C6 and C17 in **9c** *R**,*R**. Selected bond distances and angles in **9b** and **9c** are given in Tables 2 and 3, respectively.

Compounds **9b** and **9c** show octahedral geometry around the Cr atom with the hydrazinocarbene ligand acting as chelating ligand through the N1 and C5 atoms. The Cr1–C5 bond distances (2.031(4) Å in **9b**, 2.044(5) and 2.043(6) Å for A and B in **9c**) are comparable to those found in **6** (2.028(4) Å [11b]), the first structurally characterised hydrazinocarbene complex [11b]. Also the Cr1–N1 bond distances (2.208(4) Å) in **9b** and 2.208(5) and 2.216(5) Å for A and B in **9c** are strictly comparable to that observed in the starting compound **6** (2.211(4) Å).

To explain the observed diastereoselectivity, we propose two transition state models (**1** and **2**; Chart 1); the lithium ion can bring together the two reacting molecules (enone and complex anion) in a tidy transition state that leads to a high level of diastereoselectivity. A similar lithium interaction has been proposed for the Michael addition of ester enolates with unsaturated esters [19]. In models **1** and **2**, the enone's approach is from the less hindered side of the complex, far away from the nitrogen substituents; the low d.e. observed in the reaction with the cyclopentenone **7a** can be explained by the difficulty of the five-membered enone to reach a transition state such as pattern **1** because, in this case, the carbonyl group is further from the lithium ion coordinated to chromium (Chart 1).

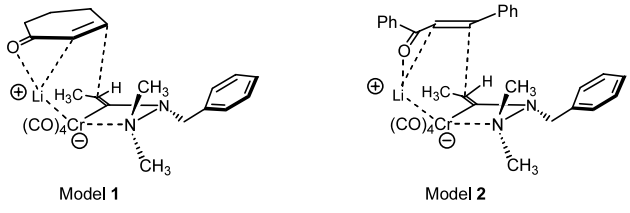
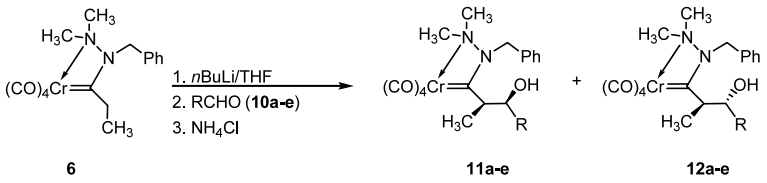


Chart 1.

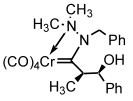
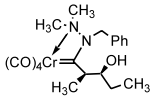
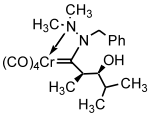
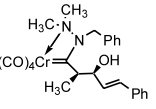
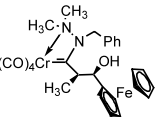
2.2. Nature of carbene complex enolates

Models **1** and **2** imply a precise configuration of the carbene enolate, which we therefore tried to clarify. Although Fischer-type carbene complex enolates are widely used in stereoselective reactions, there are few published studies of the nature of lithium enolates (which are most frequently used). X-ray structure of a potassium 18-crown-6 alkoxy carbene complex enolate



Scheme 5.

Table 4

Entry	Aldehydes	Aldols[a]	Reaction conditions[b]	d.e. (%)[c]	yield (%)	d.e. (%)[d]
1	**10a** 	**11a-12a** 	- 78 °C/30'	95	90	95
			- 78 °C/3[h]30'	95	85	95
			- 30 °C/1[h]	25	72	24
2	**10b**	**11b-12b** 	- 78 °C/30'	74	86	74
			- 78 °C/3[h]30'	73	81	74
			- 30 °C/1[h]	65	78	56
3	**10c** 	**11c-12c** 	- 78 °C/30'	91	93	93
			- 78 °C/3[h]30'	93	83	93
			- 30 °C/1[h]	58	70	57
			- 78 °C/30' 0.37 M	93	84	91
			- 78 °C/3[h]30' Kriptofix 211	70[e]	75	69[e]
4	**10d**	**11d-12d** 	- 78 °C/30'	90	80 (3)[f]	>98
			- 78 °C/3[h]30'	>98	63 (4)[f]	>98
			- 30 °C/1[h]	18	31 (17)[f]	42
5	**10e** 	**11e-12e** 	- 78 °C/30'	90	84	91
			- 78 °C/3[h]30'	52	77	54

[a]Structures of the major products (**11a**–**11e**) are shown. [b]Unless otherwise specified, the anion concentration was about 0.07 M. [c]d.e. of the crude reaction products (by NMR). [d]d.e. after purification (from the weights of the separated diastereoisomers). [e]Major product is the *anti*-isomer (**12c**). [f]Yields of the Michael addition products are in brackets.

has been reported [14], but the naked solid-state anion is not comparable with lithium salt in THF solution because of different natures of the two cations and the effect of the solvent. Furthermore, the NMR and IR spectra of the lithium and PPN [bis(triphenylphosphoranylidene)ammonium]alkoxy carbene complex enolate [15] in THF solution are identical and there are no isocarbonyl bands [16] in IR spectra, thus excluding any interaction between the cation and carbonyls of the complex [17]. It is plausible that lithium is separated from the anion in solution [15] and it may play an important role as a Lewis acid in improving the reactivity to electrophiles such as enones and aldehydes; we have observed a considerable decrease in reactivity in aldol and Michael additions when compounds capable of binding the lithium ion were added (Table 1, entries 2 and 3; Table 4, entry 3). We therefore decided to study the enolate of **6** by means of NMR. In THF-D_8 solution, an NOE experiment (Scheme 3) showed that the enolate of **6** has a *Z* configuration, that is the same as that expected for the corresponding amide enolate.

The anion was generated with *n*-BuLi at −78 °C and with a concentration analogous to the one used in the reactions. The anion of **6** is also very stable (under nitrogen atmosphere) at room temperature. The NMR spectrum does not change between −78 and 20 °C, and even in the presence of a small excess of complex **6**, no isomerisation was observed. The ^{1}H- and ^{13}C-NMR spectra (see Section 4 for more details) indicate that the enolate structure is best described as a vinyltetracarbonylchromium anion in which the negative charge is delocalised on the organometallic group (Scheme 3), a

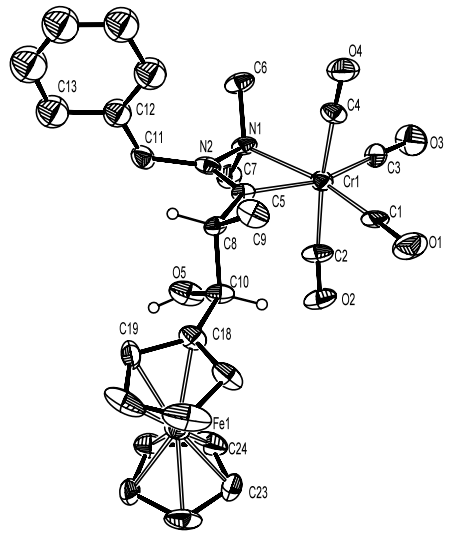


Fig. 3. View of the molecular structure of **11e** together with the atomic numbering system. Thermal ellipsoids are drown at 30% probability level.

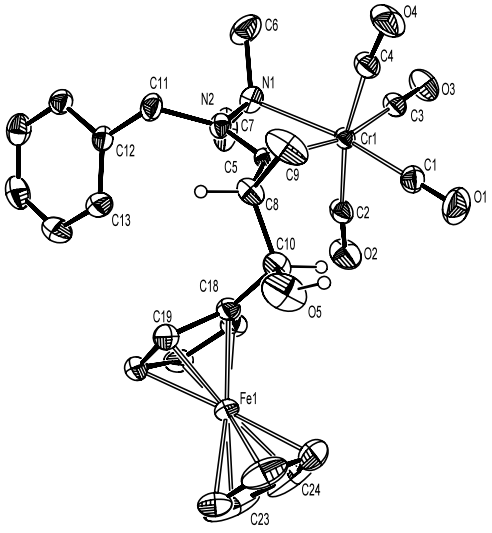


Fig. 4. View of the molecular structure of **12e** together with the atomic numbering system. Thermal ellipsoids are drown at 30% probability level.

structure that fits the diastereoselection models discussed above.

2.3. Aldol addition

The enolate generated from complex **6** reacted in aldol-type addition reactions with the aldehydes **10a**–**10e**. The chosen aldehydes are representative of different classes: aromatic (**10a**), linear aliphatic (**10b**), branched aliphatic (**10c**), α, β-unsaturated (**10d**) and organometallic-containing aldehydes (**10e**). Table 2 shows the d.e. values and chemical yields of the aldol addition products (**11a**–**11e** and **12a**–**12e**, Scheme 5).

Table 5
Selected bond lengths (Å) and angles (°) for **11e** (left) and **12e** (right)

Bond distances		
Cr(1)–N(1)	2.206(10)	2.206(3)
Cr(1)–C(5)	2.019(11)	2.051(3)
N(1)–N(2)	1.438(12)	1.461(4)
N(2)–C(5)	1.331(13)	1.304(4)
N(2)–C(11)	1.490(12)	1.483(4)
C(5)–C(8)	1.503(15)	1.502(4)
C(8)–C(9)	1.530(13)	1.530(5)
Bond angles		
C(5)–Cr(1)–N(1)	62.8(4)	62.70(11)
N(2)–N(1)–Cr(1)	89.9(7)	89.42(16)
C(5)–N(2)–N(1)	105.7(10)	106.6(2)
N(2)–C(5)–C(8)	118.1(10)	120.5(3)
N(2)–C(5)–Cr(1)	101.5(8)	101.1(2)
C(8)–C(5)–Cr(1)	140.1(9)	137.6(2)

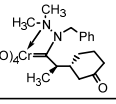
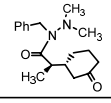
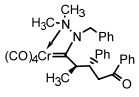
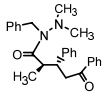
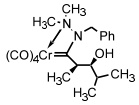
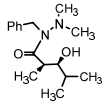
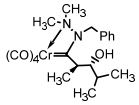
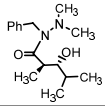
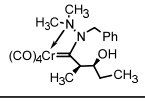
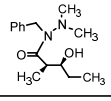
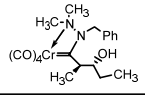
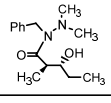
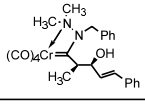
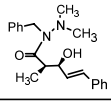
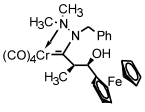
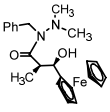
The best results were obtained by running the reactions at −78 °C for 30 min: we isolated a mixture of the two diastereoisomers **11** and **12** with very high yields and d.e. (except for aldehyde **10b**, Table 4, entry 2). The d.e. values were inferred from the ^{1}H-NMR spectra of the crude reaction mixtures. The two diastereoisomers **11** and **12** could be easily separated by column chromatography over silica gel. All the aldol adducts **11** and **12** were very stable and the d.e. values did not change after the purification step. The only exception was entry 4, in which the minor diastereoisomer **12d** is poorly stable on silica gel. At −78 °C, the reactions were not reversible and the d.e. values did not change even after longer reaction times (from 30 min to 3.5 h); entry 5 was an exception, probably because the electron-rich ferrocenyl moiety may favour a retro-aldol reaction and thus enrich the reaction mixture of the more thermodynamically stable *anti*-isomer **12e**.

The relative configurations at the two stereocentres of complexes **11e** and **12e** were determined by X-ray diffraction methods. Views of the molecular structures of the two isomeric complexes **11e** (*syn*) and **12e** (*anti*) are given in Fig. 3 and 4, respectively.

Lists of the selected bond distances and angles in the isomers are given in Table 5.

Being the structures of **11e** and **12e** centrosymmetrical, both enantiomers are present in the crystals, with the stereogenic centres C8 and C10 *R**,*S** in **11e** and *R**,*R** in **12e**. Both isomers show octahedral geometry around the Cr atom with the hydrazinocarbene ligand acting as chelating ligand through the N1 and C5 atoms. The Cr1–C5 and Cr1–N1 bond distances in the two isomers (2.019(11) and 2.206(10) Å in **11e** and 2.051(3) and 2.206(3) Å in **12e**) are in agreement with those observed in **9b**, **9c** and **6**. The orientation of the benzyl group in *syn* diastereoisomer **11e** is different from that in *anti* diastereoisomer **12e**; in the former it is disposed on the same side of the methyl atom C9, whereas in the latter it is pointing in the opposite side.

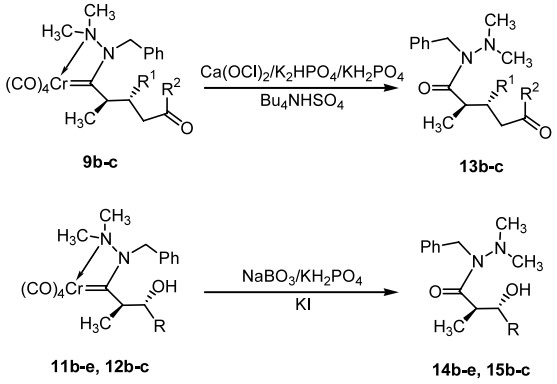
Table 6

Entry	Carbene complexes		Hydrazides		Reaction conditions	yield (%)	References[c]
1	**9b**		**13b**		a	92	
2	**9c**		**13c**		a	96.5	
3	**11c**		**14c**		b	90	[21]
4	**12c**		**15c**		b	92	[22]
5	**11b**		**14b**		b	93	[21b, 23]
6	**12b**		**15b**		b	97.6	[22, 23]
7	**11d**		**14d**		b	84	[24]
8	**11e**		**14e**		b	88	

Reaction conditions: (a) $Ca(OCl)_2/KH_2PO_4/K_2HPO_4/N(n\text{-}Bu)_4HSO_4$; (b) $NaBO_3 \cdot 4H_2O/KH_2PO_4/I_2$; (c) reference amides and *N*-hydroxyamide with an identical acidic moiety of hydrazides.

The relative configuration of complexes **11a**–**11d** and **12a**–**12d** (Table 4, entries 1-4) was assigned by ^{1}H-NMR on the basis of the characteristic coupling constant $J_{CrCCHCHOH}$ [20] (in analogy to what has been reported for similar amino carbene complex aldols 9), and by comparing the oxidation products of the carbene complexes with the isolobal organic compounds (see Table 6).

In order to obtain a larger amount of the minor diastereoisomers for analytical purposes, the reactions with aldehydes **10a**–**10d** were performed at −30 °C and led to a significant reduction in d.e.. The d.e. values in the aldol reaction with hydrazinocarbene complex **6** were not affected by the concentration of the enolate (Table 4, entry 3). The lithium ion is important in order to obtain high *syn* diastereoselectivity and a high reaction rate: when an equimolar amount of Kriptofix 221 was added to the enolate carbene complex (Table 4, entry 3), the aldol reaction was very slow (TLC clearly showed a very low reaction rate) and there was a diastereoselectivity inversion in favour of the *anti*-



Scheme 6.

diastereoisomer. The chair-like Zimmerman-Traxler models (Chart 2) can explain the formation of the major (*syn*) and minor (*anti*) diastereoisomers (the enolate configuration has been discussed above). Model **B** is less favoured than **A** because of the dominant steric interaction between the enolate *N*-benzyl group and the aldehyde axial substituent (Chart 2).

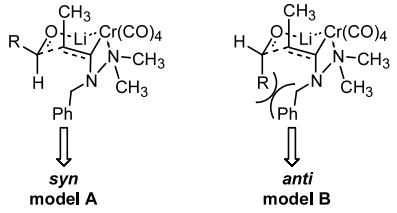


Chart 2.

2.4. Oxidations

Oxidation of the metal–carbon double bond to a carbonyl group in Fischer-type carbene complexes is still the easiest and most convenient method of recovering the organic ligand as a stable organic molecule. This transformation is generally highly efficient provided that the appropriate oxidation protocol is chosen. A very large number of different oxidation reagents and conditions have so far been published because each class of chromium carbene complexes (alkoxy, amino, hydrazino) often requires its own oxidant. Furthermore, if oxidation-sensitive substituents are present in the carbene complex structure (hydroxy group, amino group, etc.), it is necessary to select the right reaction conditions in order to prevent undesirable reactions.

During our studies of the reactivity of the penta- and tetracarbonyl hydrazinocarbene complexes **4** and **5**, we set up the best conditions for transforming hydrazinocarbenes into organic isolobal hydrazides [13].

In this study, we used these protocols to transform some of the Michael and aldol adducts into the corresponding organic hydrazides. In particular, complexes **9b**, **9c**, **11b**–**11e**, **12b** and **12c** were oxidised using two different methods: (i) in the first, the oxidant KOCl, generated in situ from $Ca(OCl)_2$ and the phosphate buffer K_2HPO_4/KH_2PO_4 under phase-transfer conditions (Scheme 6), was used to transform **9b** and **9c** into **13b** and **13c** (see Section 4); (ii) in the second, the oxidant iodine was generated in situ by means of the oxidation of KI with sodium perborate in the presence of KH_2PO_4 (Scheme 6), and gave complexes **14b**–**14e** and **15b** and **15c**.

In all cases, the δ-keto (Table 3, **13b** and **13c**, entries 1 and 2) and β-hydroxyhydrazides (Table 6, entries 3–8, **14b**–**14e** and **15b** and **15c**) were obtained in very high chemical yields as pure diastereoisomers without any epimerisation during the oxidation reactions.

The new hydrazides were fully characterised, with the ^{1}H- and ^{13}C-NMR chemical shifts and coupling constants being used to confirm the stereochemistry of the diastereoisomers. The spectroscopic data of hydrazides **13b**, **13c**, **14b**–**14e**, **15b** and **15c** were in good agreement with those of the amides and *N*-hydroxyamides derived from the same carboxylic acids present in the hydrazide structure.

3. Conclusions

The anion generated from the tetracarbonyl hydrazinocarbene complex **6** easily adds to enones and aldehydes to give the corresponding 1,4 and aldol addition products in high chemical yields and diastereoselectivity. The major diastereoisomer obtained from the Michael additions was *anti*, as determined by the X-ray analysis of adducts **9b** and **9c**. The stereochemical outcome of these reactions can be explained by considering the transition state models **1** and **2**. Enolisation of hydrazinocarbene **6** leads to the formation of the *Z* enolate, as inferred from one-dimensional NOE experiments of the anion.

The major diastereoisomer obtained in the addition of **6** to aldehydes **10a**–**10e** was the *syn*, as inferred from the X-ray analysis of a single crystal of adducts **11e** and **12e**. The stereochemical outcome of the aldol additions can be explained by considering the classical Zimmerman-Traxler transition state model.

Some of the new hydrazinocarbene complexes obtained from the Michael and aldol additions were submitted to oxidation, which led to the formation of the corresponding hydrazides in very high chemical yields, without any racemisation. These diastereoisomeric hydrazides have not been previously reported in the literature. We have thus demonstrated the usefulness of tetracarbonyl hydrazinocarbene complex **6** in the stereoselective formation of new carbon–carbon bonds, which can be attributed to the particular steric and electronic characteristics of this very stable complex.

4. Experimental

4.1. General experimental considerations

All the reactions on carbene enolates were carried out under an atmosphere of dry argon or nitrogen; the glassware was flame-dried before use. THF was dried by means of distillation over sodium wires/benzophenone before use; the butyllithium solutions were titrated before use. The $Ca(OCl)_2$ (Fluka-RdH) was technical (about 65%). Flash and vacuum chromatography were performed using Merck silica gel 60, 230–400 mesh. The melting points were determined using a Büchi 510 apparatus and are uncorrected. The diastereoselectivity of the reactions was determined by NMR of the crude products, except in the case of the synthesis of complexes **8**–**9c** in the presence of DMPU as co-solvent, in which the crude products were prepurified (in order to remove the DMPU) by means of very fast vacuum chromatography with a short column (eluent: CH_2Cl_2). The ^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) spectra were recorded using a Bruker AC 300 and Bruker AMX 300. The IR spectra were

recorded using a Perkin–Elmer FT-IR 1725X. The mass spectra (EI, FAB) were recorded using a Vg Analytical 7070 EQ.

4.2. Anion of (Z)-tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)ethylcarbene]chromium(0) (6)

^{1}H-NMR (THF-D_8, 300 MHz) δ (ppm): 7.5–6.9 (5H, m, $H_{arom.}$), 4.56 (1H, q, $J = 5.9$ Hz, CH), 3.82 (2H, s, CH_2Ph), 2.59 (6H, s, NMe_2), 1.52 (3H, d, $J = 5.9$ Hz, CHCH_3); ^{13}C-NMR DEPT (THF-D_8, 75 MHz) δ (ppm): 240.4, 232.0, 225.6 (CO), 175.8 ($C_{carbene}$), 142.9 (C_q Ph), 128.3, 127.7, 126.1 (C Ph), 93.8 (C=CH), 51.4 (NMe_2), 49.7 (CH_2Ph), 18.4 ($CHCH_3$).

4.3. Michael addition

4.3.1. Michael addition of the enolate of the tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)ethylcarbene]chromium(0) (6) with enones: general procedure

n-BuLi (solution in hexane, one equivalent) was added dropwise to a −78 °C solution of complex **6** (one equivalent) in dry THF (5 ml for 0.3 mmol of complex **6**), and the mixture was allowed to react at the same temperature for 30 min. Where stated, after 20 min at −78 °C, the mixture was warmed to −30 °C for 10 min before adding the enone; in some reactions, two or four equivalents of DMPU were added after anion formation at −78 °C. Enone (1.2 equivalents) was added and, after stirring for 3 h at −78 °C (1 h 30 min for the reactions at −30 °C), 0.25 ml of water was added at the same temperature. The organic solvent was removed in vacuo and the residue dissolved with CH_2Cl_2 and dried over Na_2SO_4. The solvent was then evaporated at reduced pressure, giving a crude red oil which was purified by flash chromatography over silica gel (15 g).

4.3.2. Synthesis of tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-(1-methyl)methylene-(3-cyclopentanone)carbene]chromium(0) (8–9a): reaction at −78 °C

Complex **6**: 103 mg (0.29 mmol, one equivalent); dry THF: 5 ml; *n*-BuLi, 1.43 M: 0.21 ml (0.30 mmol, 1.03 equivalents); cyclopentenone **7a**: 0.03 ml (0.37 mmol, 1.27 equivalents). Crude product: 153.5 mg; d.e.: 42%. After purification (eluent: Et_2O), 0.111 g of complex **1** was obtained as a mixture of diastereoisomers; d.e. after purification: 47%; yield: 87.1%.

4.3.2.1. (R*,R*) and (R*,S*)-Tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-(1-methyl)methylene-(3-cyclopentanone)carbene]chromium(0) (8–9a).

Complexes **8a** and **9a** (mixture of diastereoisomers): red viscous oil; Rf: 0.14 (eluent: Et_2O). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.5–7.1 (5H, m, H_{aromat}), 4.79 (1H, d, $J = 17.1$ Hz, CH_2Ph maj. diast.), 4.75 (1H, d, $J = 17.0$ Hz, CH_2Ph min. diast.), 4.64 (1H, d, $J = 17.1$ Hz, CH_2Ph maj. diast.), 4.60 (1H, d, $J = 17.0$ Hz, CH_2Ph min. diast.), 2.89 (3H, s, NMe_2 maj. diast.), 2.87 (3H, s, NMe_2 min. diast.), 2.81 (3H, s, NMe_2 maj. diast.), 2.79 (3H, s, NMe_2 min. diast.), 2.7–2.2 (6H, m, CrCCH + $CHCH_2COCH_2$), 1.9–1.5 (2H, m, CH_2CH_2CO), 1.41 (3H, d, $J = 4.8$ Hz, CrCCHCH_3 min. diast.), 1.34 (3H, d, $J = 6.5$ Hz, CrCCHCH_3 maj. diast.); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 294.7 ($C_{carbene}$), 231.9, 229.4, 219.4, 219.2, 218.3, 217.8, 217.2 (CO complex + CO ketone), 133.5 (Cq Ph), 129.6, 128.7, 126.1 (C Ph), 52.7, 52.3 (NMe_2), 49.4 (CH_2Ph), 49.1 (CrCCH), 44.2 ($CHCH_2CO$ min. diast.), 43.0 (CrCCHCH maj. diast.), 42.6 ($CHCH_2CO$ maj. diast.), 42.3 (CrCCHCH min. diast.), 38.7 (CH_2CH_2CO maj. diast.), 37.9 (CH_2CH_2CO min. diast.), 29.0 (CH_2CH_2CO maj. diast.), 27.0 (CH_2CH_2CO min. diast.), 18.3 (CH_3 maj. diast.), 17.2 (CH_3 min. diast.); IR/FT (neat) ν (cm^{-1}): 1998 (*trans*-CO), 1868, 1833 (*cis*-CO), 1739 (CO ketone), 737 ($\gamma CH_{arom.}$), 698 ($\delta CH_{arom.}$).

4.3.3. Synthesis of tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-(1-methyl)methylene-(3-cyclohexanone)carbene]chromium(0) (8b and 9b)

Reaction at −78 °C. Complex **6**: 103 mg (0.29 mmol, one equivalent); dry THF: 5 ml; *n*-BuLi, 1.55 M: 0.195 ml (0.30 mmol, 1.02 equivalents); 2-cyclohexen-1-one **7b**: 0.035 ml (0.36 mmol, 1.2 equivalents). Crude product: 146.5 mg; d.e.: 92%. After purification (eluent: Et_2O/AcOEt = 9/1), 7 mg of complex **8b** and 102 mg of complex **9b** were obtained; d.e. after purification: 87%; yield: 81.7%.

Reaction at −30 °C. Complex **6**: 103 mg (0.29 mmol, one equivalent); dry THF: 5 ml; *n*-BuLi, 1.35 M: 0.22 ml (0.3 mmol, 1.01 equivalents); 2-cyclohexen-1-one **7b**: 0.03 ml (0.31 mmol, 1.06 equivalents). Crude product: 123 mg; d.e.: 75%. After purification (eluent: Et_2O/AcOEt = 9/1), 12 mg of complex **8b** and 69 mg of complex **9b** were obtained; d.e. after purification: 70%; yield: 52.0%.

Reaction at −78 °C *in the presence of two equivalents of DMPU*. Complex **6**: 108 mg (0.31 mmol, one equivalent); dry THF: 5 ml; *n*-BuLi, 1.32 M: 0.24 ml (0.32 mmol, 1.03 equivalents); after 30 min, 0.075 ml of DMPU (0.62 mmol, 2.03 equivalents) was added; after 15 min, 0.035 ml of 2-cyclohexen-1-one **7b** (0.36 mmol, 1.18 equivalents) was added. Crude product: 232 mg; d.e.: 76%. After purification (eluent: Et_2O/AcOEt = 9/1), 10 mg of the complex **8b** and 109 mg of complex **9b** were obtained; d.e. after purification: 83%; yield: 86.3%.

Reaction at −78 °C *in the presence of four equivalents of DMPU*. Complex **6**: 103 mg (0.29 mmol, one equivalent); dry THF: 5 ml; *n*-BuLi, 1.55 M: 0.195 ml (0.30 mmol, 1.02 equivalents); after 30 min, 0.145 ml of

DMPU (1.2 mmol, 4.08 equivalents) was added; after 15 min, 0.035 ml of 2-cyclohexen-1-one **7b** (0.36 mmol, 1.23 equivalents) was added. Crude product: 301 mg; d.e.: 22%. After purification (eluent: Et_2O/AcOEt = 9/1), 35 mg of complex **8b** and 62 mg of complex **9b** were obtained; d.e. after purification: 27%; yield: 73.0%.

4.3.3.1. (R,S*)-Tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-(1-methyl)methylene-(3-cyclohexanone)carbene]chromium(0) (**8b**).* Complex **8b** (minor diastereoisomer): orange solid; m.p. 139 °C (Et_2O/pentane); Rf: 0.23 (eluent: Et_2O/AcOEt = 9/1). Anal. Calcd for $C_{22}H_{26}CrN_2O_5$: C, 58.66; H, 5.82; N, 6.22. Found: C, 58.33; H, 5.60; N, 6.52%. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.5–7.1 (5H, m, H_{aromat}), 4.82 (1H, d, $J = 17.0$ Hz, CH_2Ph), 4.47 (1H, d, $J = 17.0$ Hz, CH_2Ph), 2.90 (3H, s, NMe_2), 2.71 (3H, s, NMe_2), 2.75–1.70 (9H, m, CrCCH + cycloesanone), 1.18 (3H, d, $J = 6.3$ Hz, CrCCHCH_3); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 295.2 ($C_{carbene}$), 231.8, 229.4, 218.9, 218.5 (CO), 211.5 (CO ketone), 133.9 (Cq Ph), 129.4, 128.5, 126.2 (C Ph), 52.8, 52.1 (NMe_2), 49.8 (CH_2Ph), 46.9 (CHCH_2CO), 44.8 (CrCCH), 43.1 (CrCCHCH), 41.5 (CH_2CH_2CO), 26.6 (CH_2CH_2CO), 23.5 (CHCH_2CH_2), 16.8 (CH_3). IR/FT (neat) ν (cm^{-1}): 1997 (*trans*-CO), 1868, 1829 (*cis*-CO), 1709 (CO ketone), 728 ($\gamma CH_{arom.}$), 682 ($\delta CH_{arom.}$). MS (FAB^+), *m/z* 450 [M^+], 422 [M^+–CO], 366 [M^+–3CO], 338 [M^+–4CO], 293 [M^+–4CO–$HNMe_2$], 247 [M^+–4CO–$PhCH_2$], 91 [$C_7H_7^+$].

4.3.3.2. (R,R*)-Tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-(1-methyl)methylene-(3-cyclohexanone)carbene]chromium(0) (**9b**).* Data for complex **9b** (major diastereoisomer): orange solid; m.p. 129 °C (CH_2Cl_2/pentane); Rf: 0.18 (eluent: Et_2O/AcOEt = 9/1). Anal. Calcd for $C_{22}H_{26}CrN_2O_5$: C, 58.66; H, 5.82; N, 6.22. Found: C, 58.82; H, 5.70; N, 6.09%. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.5–7.1 (5H, m, H_{aromat}), 4.76 (1H, d, $J = 17.0$ Hz, CH_2Ph), 4.55 (1H, d, $J = 17.0$ Hz, CH_2Ph), 2.84 (3H, s, NMe_2), 2.72 (3H, s, NMe_2), 2.7–2.6 (1H, m, CrCCH), 2.45–1.6 (9H, m, cycloesanone), 1.23 (3H, d, $J = 6$ Hz, CrCCHCH_3); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 295.6 ($C_{carbene}$), 232.0, 229.9, 219.7, 218.9 (CO), 210.5 (CO ketone), 133.9 (Cq Ph), 130.0, 129.2, 126.6 (C Ph), 52.6, 52.1 (NMe_2), 49.9 (CH_2Ph), 49.2 (CrCCH), 45.3 (CHCH_2CO), 44.0 (CrCCHCH), 41.8 (CH_2CH_2CO), 31.5 (CH_2CH_2CO), 24.9 (CHCH_2CH_2), 17.3 (CH_3). IR/FT (neat) ν (cm^{-1}): 1996 (*trans*-CO), 1844 (*cis*-CO), 1708 (CO ketone), 736 ($\gamma CH_{arom.}$), 686 ($\delta CH_{arom.}$). MS (FAB^+), *m/z* 450 [M^+], 378 [M^+–CO–NMe_2], 338 [M^+–4CO], 293 [M^+–4CO–$HNMe_2$], 247 [M^+–4CO–$PhCH_2$], 91 [$C_7H_7^+$].

*4.3.4. Synthesis of tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-(2,4-diphenyl-1-methyl-4-oxo)butylcarbene]chromium(0) (**8c** and **9c**)*

Reaction at −78 °C. Complex **6**: 103 mg (0.29 mmol, one equivalent); dry THF: 5 ml; *n*-BuLi, 1.55 M: 0.19 ml (0.29 mmol, 1.02 equivalents); 1,3-diphenyl-propenone **7c**: 73 mg (0.35 mmol, 1.21 equivalents). Crude product: 184.5 mg; d.e.: 98%. After purification (eluent: Et_2O/AcOEt = 9/1), 96.5 mg of complex **9c** was obtained; d.e. after purification > 98%; yield: 59.6%.

Reaction at −78 °C *in the presence of four equivalents of DMPU*. Complex **6**: 103 mg (0.29 mmol, one equivalent); dry THF: 2 ml; *n*-BuLi, 1.55 M: 0.195 ml (0.30 mmol, 1.03 equivalents); after 30 min, 0.145 ml of DMPU (1.2 mmol, 4.12 equivalents) was added; after 15 min, 72 mg of 1,3-diphenyl-propenone **7c** (0.35 mmol, 1.19 equivalents) was added. Crude product: 327 mg; d.e. after prepurification: 89%. After purification (eluent: Et_2O/ETP = 7/3), 5 mg of complex **8c** and 93 mg of complex **9c** were obtained; d.e. after purification: 90%; yield: 59.5%.

Reaction at −78 °C *in DMPU as co-solvent*. Complex **6**: 103 mg (0.29 mmol, one equivalent); dry THF: 5 ml; *n*-BuLi, 1.55 M: 0.19 ml (0.29 mmol, 1.02 equivalents); after 30 min, 3 ml of DMPU (24.9 mmol, 86.4 equivalents) were added; after 15 min, 0.0731 of 1,3-diphenyl-propenone **7c** (0.35 mmol, 1.22 equivalents) were added. d.e. after prepurification: 74%. After purification (eluent: Et_2O/ETP = 7/3), 54 mg of complex **6** (yield of recovery: 53.1%), 5 mg of complex **8c** and 35 mg of complex **9c** were obtained; d.e. after purification: 75%; yield: 24.7%.

Reaction at −30 °C *in the presence of four equivalents of DMPU*. Complex **6**: 103 mg (0.29 mmol, one equivalent); dry THF: 5 ml; *n*-BuLi, 1.55 M: 0.19 ml (0.29 mmol, 1.02 equivalents); after 20 min, 0.140 ml of DMPU (1.16 mmol, four equivalents) was added; after 10 min, at −30 °C 72 mg of 1,3-diphenyl-propenone **7c** (0.34 mmol, 1.19 equivalents) was added; d.e. after prepurification: 90%. After purification (eluent: Et_2O/ETP = 7/3), 6 mg of complex **8c** and 94 mg of complex **9c** were obtained; d.e. after purification: 88%; yield: 61.8%.

4.3.4.1. (R,S*)-Tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-(2,4-diphenyl-1-methyl-4-oxo)butylcarbene]chromium(0) (**8c**).* Complex **8c** (minor diastereoisomer): orange solid; m.p. 141 °C (CH_2Cl_2/pentane); Rf: 0.17 (eluent: ETP/AcOEt = 4/6). Anal. Calcd for $C_{31}H_{30}CrN_2O_5$: C, 66.18; H, 5.37; N, 4.98. Found: C, 65.92; H, 5.53; N, 4.72%. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.9–7.0 (15H, m, H_{aromat}), 4.17 (1H, d, $J = 17.2$ Hz, CH_2Ph), 4.08 (1H, d, $J = 17.2$ Hz, CH_2Ph), 3.9–3.75 (1H, m, CHCHPh), 3.75–3.6 (2H, m, CH_2CO), 3.06 (1H, q, $J = 6.6$ Hz, CH_3CH), 2.82 (3H, s, NMe_2), 2.64 (3H, s, NMe_2), 1.31 (1H, d, $J =$

6.5 Hz, CH_3CH); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 295.3 ($C_{carbene}$), 232.2, 229.7, 220.9, 218.5 (CO), 199.0 (CO ketone), 142.6, 137.6, 134.4 (Cq Ph), 134–125 (C Ph), 52.8 (NMe_2), 49.6 (CH_2Ph), 48.8 (CrCCH), 47.9 (CHPh), 40.6 (CH_2CO), 17.5 (CH_3). IR/FT (Nujol) ν (cm^{-1}): 1996 (*trans*-CO), 1892, 1841 (*cis*-CO), 1684 (CO ketone), 740 ($\gamma CH_{arom.}$), 680 ($\delta CH_{arom.}$).

4.3.4.2. (R,R*)-Tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-(2,4-diphenyl-1-methyl-4-oxo)butylcarbene]chromium(0) (**9c**).* Complex **9c** (major diastereoisomer): orange solid; m.p. 141 °C (CH_2Cl_2/pentane); Rf: 0.24 (eluent: ETP/AcOEt = 4/6). Anal. Calcd for $C_{31}H_{30}CrN_2O_5$: C, 66.18; H, 5.37; N, 4.98. Found: C, 65.92; H, 5.53; N, 4.72%. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.85–6.85 (15H, m, H_{aromat}), 4.21 (1H, d, $J = 17.2$ Hz, CH_2Ph), 3.98 (1H, d, $J = 17.2$ Hz, CH_2Ph), 3.84 (1H, td, $J_1 = 10.0$ Hz, $J_2 = 4.0$ Hz, CHCHPh), 3.71 (1H, dd, $J_{gem} = 16.1$ Hz, $J_{vic} = 4.0$ Hz, CH_2CO), 3.29 (1H, dd, $J_{gem} = 16.1$ Hz, $J_{vic} = 10.0$ Hz, CH_2CO), 3.00 (1H, dq, $J_1 = 10.0$ Hz, $J_2 = 6.5$ Hz, CH_3CH), 2.53 (3H, s, NMe_2), 2.49 (3H, s, NMe_2), 1.53 (1H, d, $J = 6.5$ Hz, CH_3CH); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 293.8 ($C_{carbene}$), 232.6, 229.9, 220.0, 219.5 (CO), 198.7 (CO ketone), 143.1, 137.4, 134.2 (Cq Ph), 133.4, 129.9, 129.0, 128.9, 128.5, 127.6, 126.9, 126.4 (C Ph), 52.9, 52.4 (NMe_2), 49.6 (CH_2Ph), 49.0 (CrCCH), 45.9 (CHPh), 42.1 (CH_2CO), 18.7 (CH_3). IR/FT (neat) ν (cm^{-1}): 1997 (*trans*-CO), 1864 (*cis*-CO), 1685 (CO ketone), 736 ($\gamma CH_{arom.}$), 688 ($\delta CH_{arom.}$).

*4.3.5. Synthesis of tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-(1,4-dimethyl-2-phenyl-4-oxo)butylcarbene]chromium(0) (**9d**): reaction at −78 °C*

Complex **6**: 103 mg (0.29 mmol, one equivalent); dry THF: 5 ml; *n*-BuLi, 1.503 M: 0.195 ml (0.29 mmol, 1.02 equivalents); 4-phenyl-but-3-en-2-one **7d**: 51 mg (0.35 mmol, 1.22 equivalents). Crude product: 185 mg; d.e. > 98%. After purification (eluent: Et_2O/AcOEt = 9/1), 125 mg of complex **9d** was obtained; d.e. after purification > 98%; yield: 86.7%.

4.3.5.1. (R,R*)-Tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-(1,4-dimethyl-2-phenyl-4-oxo)butylcarbene]chromium(0) (**9d**).* Complex **9d**: orange solid; m.p. 119 °C (Et_2O/pentane). Anal. Calcd for $C_{26}H_{28}CrN_2O_5$: C, 62.39; H, 5.64; N, 5.60. Found: C, 62.25; H, 5.50; N, 5.71%. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.4–6.9 (10H, m, H_{aromat}), 4.20 (1H, d, $J =$ 17.2 Hz, CH_2Ph), 4.02 (1H, d, $J = 17.2$ Hz, CH_2Ph), 3.70 (1H, td, $J_1 = 10.0$ Hz, $J_2 = 4.4$ Hz, CHCHPh), 3.13 (1H, dd, $J_{gem} = 15.8$ Hz, $J_{vic} = 4.4$ Hz, CH_2CO), 2.93 (1H, dq, $J_1 = 10.0$ Hz, $J_2 = 6.5$ Hz, CH_3CH), 2.83 (1H, dd, $J_{gem} = 15.8$ Hz, $J_{vic} = 10.0$ Hz, CH_2CO), 2.59 (3H, s, NMe_2), 2.55 (3H, s, NMe_2), 2.04 (3H, s, CH_3CO), 1.49 (1H, d, $J = 6.5$ Hz, CH_3CH); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 294.0 ($C_{carbene}$), 232.5, 229.8, 220.2, 219.3 (CO), 207.3 (CO ketone), 142.9, 134.1 (Cq Ph), 129.9, 129.1, 128.9, 127.7, 126.3 (C Ph), 52.9, 52.4 (NMe_2), 49.5 (CH_2Ph), 49.0 (CrCCH), 47.2 (CH_2CO), 45.7 (CHPh), 30.6 (CH_3CO), 18.6 (CHCH_3). IR/FT (neat) ν (cm^{-1}): 1998 (*trans*-CO), 1874, 1836 (*cis*-CO), 1712 (CO ketone), 738 ($\gamma CH_{arom.}$), 689 ($\delta CH_{arom.}$).

4.4. Aldol additions

*4.4.1. Aldol addition of the enolate of the tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)ethylcarbene]chromium(0) (**6**) with aldehydes: general procedure*

The procedure was similar to that of the Michael reactions with the following differences: about 4 ml of dry THF per 0.3 mmol of complex **6** and two equivalents of aldehyde were used; the reactions were quenched after 3 h 30 min or 30 min at −78 °C and after 1 h at −30 °C; where stated, a more concentrated solution of complex **6** was used; in one reaction, Kriptofix 211 was added after anion formation at −78 °C.

*4.4.2. Synthesis of the tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-1-(ethyl-1-methyl-2-phenyl-2-hydroxy)carbene]chromium(0) (**11a** and **12a**)*

Reaction at −78 °C for 30 min. Complex **6**: 108 mg (0.31 mmol, one equivalent); dry THF: 4 ml; *n*-BuLi, 1.64 M: 0.19 ml (0.31 mmol, 1.02 equivalents); benzaldehyde **10a**: 0.065 ml (0.64 mmol, 2.1 equivalents). Crude product: 160 mg; d.e.: 95%. After purification (eluent: CH_2Cl_2/ETP = 8/2), 3 mg of complex **12a** and 123.5 mg of complex **11a** were obtained; d.e. after purification: 95%; yield: 90.1%.

Reaction at −78 °C for 3 h 30 min. Complex **6**: 108 mg (0.31 mmol, one equivalent); dry THF: 4 ml; *n*-BuLi, 1.64 M: 0.19 ml (0.31 mmol, 1.02 equivalents); benzaldehyde **10a**: 0.065 ml (0.64 mmol, 2.1 equivalents). Crude product: 160 mg; d.e.: 95%. After purification (eluent: CH_2Cl_2/ETP = 8/2), 3 mg of complex **12a** and 116 mg of complex **11a** were obtained; d.e. after purification: 95%; yield: 84.8%.

Reaction at −30 °C. Complex **6**: 108 mg (0.31 mmol, one equivalent); dry THF: 4 ml; *n*-BuLi, 1.64 M: 0.19 ml (0.31 mmol, one equivalent); benzaldehyde **10a**: 0.065 ml (0.64 mmol, 2.1 equivalents). Crude product: 150 mg; d.e.: 25%. After purification (eluent: CH_2Cl_2/ETP = 8/2), 39 mg of complex **12a** and 64 mg of complex **11a** were obtained; d.e. after purification: 24%; yield: 71.7%.

4.4.2.1. (R,R*)-Tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-1-(ethyl-1-methyl-2-phenyl-2-hydroxy)carbene]chromium(0) (**11a**).* Complex **11a** (major diastereoisomer): red viscous oil; Rf: 0.2 (eluent:

ETP/CH_2Cl_2 = 2/8). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.5–6.9 (10H, m, H_{aromat}), 5.08 (1H, dd, J_1 = 8 Hz, J_2 = 2.2 Hz, OHC*H*Ph), 4.19 (2H, s, CH_2Ph), 2.99 (1H, dq, J_1 = 8 Hz, J_2 = 6.2 Hz, CrCC*H*CH_3), 2.67, 2.58 (6H, s, NMe_2), 2.43 (1H, d br., J = 2.2 Hz, OH), 1.57 (3H, d, J = 6.2 Hz, CrCCHC*H*$_3$); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 291.9 ($C_{carbene}$), 231.5, 229.3, 219.4, 218.3 (CO), 142.5 (Cq CHOH*Ph*), 133.5 (Cq NCH_2*Ph*), 129.5–125.9 (C Ph), 75.8 (CHOH), 52.2, 52.0 (NMe_2), 51.7 (CrC*C*H), 49.1 (N*C*H_2Ph), 16.0 (CrCCH*C*H_3); IR/FT (neat) ν (cm^{-1}): 3392 (OH), 1998 (*trans*-CO), 1869, 1829 (*cis*-CO), 728 ($\gamma$$CH_{arom.}$), 679 ($\delta$$CH_{arom.}$); MS (FAB$^+$), *m*/*z* 460 [$M^+$], 432 [$M^+$–CO], 376 [$M^+$–3CO], 348 [$M^+$–4CO], 303 [$M^+$–4CO–$HNMe_2$], 257 [$M^+$–4CO–$PhCH_2$], 197 [$M^+$–4CO–$HNMe_2$–PhCHO], 107 [PhCH=$OH^+$], 91 [$C_7H_7^+$].

4.4.2.2. (R,S*)-Tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-1-(ethyl-1-methyl-2-phenyl-2-hydroxy)carbene]chromium(0) (**12a**).* Complex **12a** (minor diastereoisomer): red viscous oil; Rf: 0.31 (eluent: ETP/CH_2Cl_2 = 2/8). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.5–7.2 (10H, m, H_{aromat}), 5.11 (1H, d, J = 17.2 Hz, CH_2Ph), 5.10 (1H, dd, J_1 = 9.4 Hz, J_2 = 2.8 Hz, OHC*H*Ph), 4.65 (1H, d, J = 17.2 Hz, CH_2Ph), 2.91 (3H, s, NMe_2), 2.90 (1H, dq, J_1 = 9.4 Hz, J_2 = 6.6 Hz, CrCC*H*CH_3), 2.78 (3H, s, NMe_2), 2.30 (1H, d br., J = 2.8 Hz, OH), 1.08 (3H, d, J = 6.6 Hz, CrCCHC*H*$_3$); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 292.5 ($C_{carbene}$), 232.3, 229.6, 219.1, 218.6 (CO), 141.7 (Cq CHOH*Ph*), 134.0 (Cq NCH_2*Ph*), 129.5–126.2 (C Ph), 79.1 (CHOH), 52.8, 52.1 (NMe_2), 50.7 (CrC*C*H), 49.3 (N*C*H_2Ph), 16.2 (CrCCH*C*H_3); IR/FT (neat) ν (cm^{-1}): 3431 (OH), 1998 (*trans*-CO), 1869, 1827 (*cis*-CO), 728 ($\gamma$$CH_{arom.}$), 680 ($\delta$$CH_{arom.}$), MS (FAB$^+$), *m*/*z* 460 [$M^+$], 432 [$M^+$–CO], 404 [$M^+$–2CO], 376 [$M^+$–3CO], 348 [$M^+$–4CO], 303 [$M^+$–4CO–$HNMe_2$], 257 [$M^+$–4CO–$PhCH_2$], 197 [$M^+$–4CO–$HNMe_2$–PhCHO], 91 [$C_7H_7^+$].

*4.4.3. Synthesis of tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-1-(butyl-1-methyl-2-hydroxy)carbene]chromium(0) (**11b** and **12b**)*

Reaction at −78 °C *for 3 h 30 min*. Complex **6**: 103 mg (0.29 mmol, one equivalent); dry THF: 4 ml; *n*-BuLi, 1.64 M: 0.18 ml (0.29 mmol, 1.02 equivalents); propionaldehyde **10b**: 0.045 ml (0.62 mmol, 2.1 equivalents). Crude product: 140 mg; d.e.: 73%. After purification (eluent: CH_2Cl_2/ETP = 8/2), 13 mg of complex **12b** and 84 mg of complex **11b** were obtained; d.e. after purification: 74%; yield: 81.2%.

Reaction at −78 °C *for 30 min*. Complex **6**: 106 mg (0.3 mmol, one equivalent); dry THF: 4 ml; *n*-BuLi, 1.54 M: 0.20 ml (0.31 mmol, 1.03 equivalents); propionaldehyde **10b**: 0.045 ml (0.62 mmol, 2.07 equivalents). Crude product: 134 mg; d.e.: 74%. After purification (eluent: CH_2Cl_2/ETP = 8/2), 14 mg of complex **12b** and 92 mg of complex **11b** were obtained; d.e. after purification: 74%; yield: 86.3%.

Reaction at −30 °C. Complex **6**: 103 mg (0.29 mmol, one equivalent); dry THF: 4 ml; *n*-BuLi, 1.61 M: 0.19 ml (0.31 mmol, 1.05 equivalents); propionaldehyde **10b**: 0.045 ml (0.62 mmol, 2.12 equivalents). Crude product: 135 mg; d.e.: 65%. After purification (eluent: CH_2Cl_2/ETP = 8/2), 16 mg of complex **12b** and 77 mg of complex **11b** were obtained; d.e. after purification: 66%; yield: 77.7%.

4.4.3.1. (R,S*)-Tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-1-(butyl-1-methyl-2-hydroxy)carbene]chromium(0) (**11b**).* Complex **11b** (major diastereoisomer): yellow solid; m.p. 114 °C (CH_2Cl_2/pentane). Anal. Calcd for $C_{19}H_{24}CrN_2O_5$: C, 55.34; H, 5.87; N, 6.79. Found: C, 55.52; H, 6.02; N, 6.91%. Rf: 0.04 (eluent: ETP/CH_2Cl_2 = 2/8). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.5–7.1 (5H, m, H_{aromat}), 4.80 (1H, d, J = 17 Hz, CH_2Ph), 4.62 (1H, d, J = 17 Hz, CH_2Ph), 4.0–3.8 (1H, m, HOC*H*CH_2), 2.86, 2.80 (6H, s, NMe_2), 2.62 (1H, quint., J = 6.6 Hz, CrCC*H*CH_3), 2.1 (1H, s br., OH), 1.65 (1H, ddq, J_{vic} = 2.3 Hz, J_{gem} = 13.6 Hz, J_{vic} = 7 Hz, HOCHC*H*$_2$), 1.41 (3H, d, J = 6.6 Hz, CrCCHC*H*$_3$), 1.34 (1H, ddq, J_{vic} = 2.3 Hz, J_{gem} = 13.6 Hz, J_{vic} = 7 Hz, HOCHC*H*$_2$), 1.20 (3H, t, J = 7 Hz, CH_2C*H*$_3$); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 293.0 ($C_{carbene}$), 231.5, 229.4, 218.8, 218.2 (CO), 133.5 (Cq NCH_2*Ph*), 129.4, 128.6, 126.2 (C Ph), 76.2 (CHOH), 52.5, 52.3 (NMe_2), 50.0 (CrC*C*H), 49.4 (N*C*H_2Ph), 29.1 (*C*H_2CH_3), 15.5 (CrCCH*C*H_3), 10.5 (CH_2*C*H_3); IR/FT (Nujol) ν (cm^{-1}): 3383 (OH), 2003 (*trans*-CO), 1879, 1806 (*cis*-CO), 741 ($\gamma$$CH_{arom.}$), 680 ($\delta$$CH_{arom.}$), MS (FAB$^+$), *m*/*z* 412 [$M^+$], 384 [$M^+$–CO], 356 [$M^+$–2CO], 328 [$M^+$–3CO], 300 [$M^+$–4CO], 255 [$M^+$–4CO–$HNMe_2$], 209 [$M^+$–4CO–$PhCH_2$], 165 [$M^+$–4CO–$NMe_2$–$PhCH_2$], 91 [$C_7H_7^+$].

4.4.3.2. (R,R*)-Tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-1-(butyl-1-methyl-2-hydroxy)carbene]chromium(0) (**12b**).* Complex **12b** (minor diastereoisomer): red oil. Rf: 0.1 (eluent: ETP/CH_2Cl_2 = 2/8). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.5–7.1 (5H, m, H_{aromat}), 4.99 (1H, d, J = 17.2 Hz, CH_2Ph), 4.59 (1H, d, J = 17.2 Hz, CH_2Ph), 4.2–4.0 (1H, m, HOC*H*CH_2), 2.86, 2.74 (6H, s, NMe_2), 2.67 (1H, dq, J_1 = 9.2 Hz, J_2 = 6.5 Hz, CrCC*H*CH_3), 2.06 (1H, d, J = 4.2 Hz, OH), 1.80 (1H, ddq, J_{vic} = 2.8 Hz, J_{gem} = 14.2 Hz, J_{vic} = 7.4 Hz, HOCHC*H*$_2$), 1.5–1.35 (1H, m, HOCHC*H*$_2$), 1.28 (3H, d, J = 6.5 Hz, CrCCHC*H*$_3$), 0.99 (3H, t, J = 7.4 Hz, CH_2C*H*$_3$); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 292.7 ($C_{carbene}$), 231.9, 229.4, 218.4 (CO), 133.9 (Cq NCH_2*Ph*), 129.4, 128.4, 126.1 (C Ph), 76.5 (CHOH), 52.9, 52.2 (NMe_2), 49.3 (N*C*H_2Ph), 48.6 (CrC*C*H), 26.8 (*C*H_2CH_3), 15.9

(CrCCH*C*H$_3$), 9.1 (CH$_2$*C*H$_3$); IR/FT (neat) ν (cm^{-1}): 3463 (OH), 1998 (*trans*-CO), 1866 (*cis*-CO), 728 (γCH$_{arom.}$), 680 (δCH$_{arom.}$); MS (FAB$^+$) *m/z* 412 [M$^+$], 384 [M$^+$–CO], 356 [M$^+$–2CO], 328 [M$^+$–3CO]; 300 [M$^+$–4CO], 255 [M$^+$–4CO–HNMe$_2$], 209 [M$^+$–4CO–PhCH$_2$], 165 [M$^+$–4CO–NMe$_2$–PhCH$_2$], 91 [C$_7$H$_7^+$].

4.4.4. Synthesis of tetracarbonyl[(*N*-benzyl-*N*′,*N*′-dimethylhydrazinyl)-1-(butyl-1,3-dimethyl-2-hydroxy)carbene]chromium(0) (**11c** and **12c**)

Reaction at −78 °C *for 3 h 30 min*. Complex **6**: 103 mg (0.29 mmol, one equivalent); dry THF: 4 ml; *n*-BuLi, 1.64 M: 0.18 ml (0.29 mmol, 1.01 equivalents); isobutyraldehyde **10c**: 0.055 ml (0.60 mmol, 2.06 equivalents). Crude product: 154 mg; d.e.: 93%. After purification (eluent: CH$_2$Cl$_2$/ETP = 8/2), 4 mg of complex **12c** and 100 mg of complex **11c** were obtained; d.e. after purification: 93%; yield: 83.3%.

Reaction at −78 °C *for 30 min* (concentration of carbene enolate: 0.071 M). Complex **6**: 103 mg (0.29 mmol, one equivalent); dry THF: 4 ml; *n*-BuLi, 1.52 M: 0.19 ml (0.29 mmol, one equivalent); isobutyraldehyde **10c**: 0.055 ml (0.60 mmol, 2.1 equivalents). Crude product: 128 mg; d.e.: 91%. After purification (eluent: CH$_2$Cl$_2$/ETP = 8/2), 4 mg of complex **12c** and 109 mg of complex **11c** were obtained; d.e. after purification: 93%; yield: 92.6%.

Reaction at −78 °C *for 30 min* (concentration of carbene enolate: 0.3 M). Complex **6**: 400 mg (1.13 mmol, one equivalent); dry THF: 3 ml; *n*-BuLi, 1.54 M: 0.74 ml (1.14 mmol, 1.01 equivalents); isobutyraldehyde **10c**: 0.205 ml (2.26 mmol, two equivalents). Crude product: 529 mg; d.e.: 93%. After purification (eluent: CH$_2$Cl$_2$/ETP = 8/2), 18 mg of complex **12c** and 386 mg of complex **11c** were obtained; d.e. after purification: 91%; yield: 83.7%.

Reaction at −78 °C *for 3 h 30 min in the presence of Kriptofix 221*. Complex **6**: 106 mg (0.3 mmol, one equivalent); dry THF: 3 ml; *n*-BuLi, 1.544 M: 0.2 ml (0.3 mmol, one equivalent). After anion formation, 1 ml of Kriptofix 221 solution in THF (100 mg, 90%, 0.31 mmol, one equivalent) was added; isobutyraldehyde **10c**: 0.055 ml (0.6 mmol, two equivalents). Crude product: 277 mg; d.e.: 70%. After purification (eluent: CH$_2$Cl$_2$/ETP = 8/2), 81 mg of complex **12c** and 14.5 mg of complex **11c** were obtained; d.e. after purification: 69%; yield: 75%. The reaction was slower than the same reaction without Kriptofix (TLC monitoring).

Reaction at −30 °C. Complex **6**: 100 mg (0.28 mmol, one equivalent); dry THF: 4 ml; *n*-BuLi, 1.64 M: 0.18 ml (0.3 mmol, 1.05 equivalents); isobutyraldehyde **10c**: 0.055 ml (0.60 mmol, 2.14 equivalents). Crude product: 135 mg; d.e.: 58%. After purification (eluent: CH$_2$Cl$_2$/ETP = 8/2), 18 mg of complex **12c** and 66 mg of complex **11c** were obtained; d.e. after purification: 57%; yield: 70%.

4.4.4.1. (*R**,*S**)-Tetracarbonyl[(*N*-benzyl-*N*′,*N*′-dimethylhydrazinyl)-1-(butyl-1,3-dimethyl-2-hydroxy)carbene]chromium(0) (**11c**).

Complex **11c** (major diastereoisomer): yellow solid; m.p. 130 °C (CH$_2$Cl$_2$/pentane). Anal. Calcd for C$_{20}$H$_{26}$CrN$_2$O$_5$: C, 56.33; H, 6.15; N, 6.57. Found: C, 56.25; H, 6.36; N, 6.91%. Rf: 0.08 (eluent: ETP/CH$_2$Cl$_2$ = 2/8). ^{1}H-NMR (CDCl$_3$, 300 MHz) δ (ppm): 7.5–7.05 (5H, m, H$_{aromat}$), 4.73 (1H, d, J = 17 Hz, C*H*$_2$Ph), 4.65 (1H, d, J = 17 Hz, C*H*$_2$Ph), 3.89 (1H, d br., J = 6.6 Hz, HOC*H*CH), 2.86, 2.83 (6H, s, NMe$_2$), 2.73 (1H, quint., J = 6.6 Hz, CrCC*H*CH$_3$), 2.06 (1H, s br., OH), 1.78 (1H, set.d, J_1 = 2.9 Hz, J_2 = 6.7 Hz, HOCHC*H*), 1.33 (3H, d, J = 6.6 Hz, CrCCHC*H*$_3$), 1.00 (3H, d, J = 6.7 Hz, CH(C*H*$_3$)$_2$), 0.82 (3H, d, J = 6.7 Hz, CH(C*H*$_3$)$_2$); ^{13}C-NMR DEPT (CDCl$_3$, 75 MHz) δ (ppm): 293.7 (C$_{carbene}$), 231.1, 229.4, 218.7, 218.2 (CO), 133.4 (Cq NCH$_2$*Ph*), 129.5, 128.7, 126.2 (C Ph), 78.4 (CHOH), 52.5, 52.3 (NMe$_2$), 49.6 (N*C*H$_2$Ph), 46.8 (CrC*C*H), 31.4 (*C*H(CH$_3$)$_2$), 20.2 (CrCCH*C*H$_3$), 15.5, 14.8 (CH(*C*H$_3$)$_2$); IR/FT (Nujol) ν (cm^{-1}): 3393 (OH), 1999 (*trans*-CO), 1890, 1861, 1821 (*cis*-CO), 734 (γCH$_{arom.}$), 680 (δCH$_{arom.}$); MS (FAB$^+$) *m/z* 426 [M$^+$], 398 [M$^+$–CO], 370 [M$^+$–2CO], 342 [M$^+$–3CO], 326 [M$^+$–2CO–NMe$_2$], 314 [M$^+$–4CO], 307 [M$^+$–CO–PhCH$_2$], 298 [M$^+$–3CO–NMe$_2$], 270 [M$^+$–4CO–NMe$_2$], 197 [M$^+$–4CO–HNMe$_2$–(CH$_3$)$_2$CHCHO], 179 [M$^+$–4CO–PhCH$_2$–NMe$_2$], 107 [M$^+$–4CO–HNMe$_2$–PhCH$_2$–(CH$_3$)$_2$CHCHO], 91 [C$_7$H$_7^+$].

4.4.4.2. (*R**,*R**)-Tetracarbonyl[(*N*-benzyl-*N*′,*N*′-dimethylhydrazinyl)-1-(butyl-1,3-dimethyl-2-hydroxy)carbene]chromium(0) (**12c**).

Complex **12c** (minor diastereoisomer): orange solid; m.p. 120 °C (CH$_2$Cl$_2$/pentane). Anal. Calcd for C$_{20}$H$_{26}$CrN$_2$O$_5$: C, 56.33; H, 6.15; N, 6.57. Found: C, 55.92; H, 5.99; N, 6.36%. Rf: 0.12 (eluent: ETP/CH$_2$Cl$_2$ = 2/8). ^{1}H-NMR (CDCl$_3$, 300 MHz) δ (ppm): 7.5–7.15 (5H, m, H$_{aromat}$), 4.98 (1H, d, J = 17.1 Hz, C*H*$_2$Ph), 4.58 (1H, d, J = 17.1 Hz, C*H*$_2$Ph), 4.01 (1H, ddd, J_1 = 9.5 Hz, J_2 = 4.4 Hz, J_3 = 2 Hz, HOC*H*CH), 2.87 (3H, s, NMe$_2$), 2.76 (1H, dq, J_1 = 9.5 Hz, J_2 = 6.5 Hz, CrCC*H*CH$_3$), 2.75 (3H, s, NMe$_2$), 2.00 (1H, set.d, J_1 = 2 Hz, J_2 = 6.9 Hz, HOCHC*H*), 1.83 (1H, d, J = 4.4 Hz, OH), 1.24 (3H, d, J = 6.5 Hz, CrCCHC*H*$_3$), 1.05 (3H, d, J = 6.9 Hz, CH(C*H*$_3$)$_2$), 0.77 (3H, d, J = 6.9 Hz, CH(C*H*$_3$)$_2$); ^{13}C-NMR DEPT (CDCl$_3$, 75 MHz) δ (ppm): 293.1 (C$_{carbene}$), 232.1, 229.5, 219.5, 218.5 (CO), 134.1 (Cq NCH$_2$*Ph*), 129.4, 128.4, 126.2 (C Ph), 79.1 (CHOH), 52.8, 52.1 (NMe$_2$), 49.4 (N*C*H$_2$Ph), 46.3 (CrC*C*H), 28.7 (*C*H(CH$_3$)$_2$), 20.1 (CrCCH*C*H$_3$), 15.3, 13.8 (CH(*C*H$_3$)$_2$); IR/FT (neat) ν (cm^{-1}): 3468 (OH), 1997

(*trans*-CO), 1865 (*cis*-CO), 730 ($\gamma CH_{arom.}$), 679 ($\delta CH_{arom.}$); MS (FAB$^+$) *m/z* 426 [M$^+$], 398 [M$^+$–CO], 370 [M$^+$–2CO], 342 [M$^+$–3CO], 314 [M$^+$–4CO], 307 [M$^+$–CO–PhCH$_2$], 299 [M$^+$–3CO–CH$_2$=Nme], 269 [M$^+$–4CO–HNMe$_2$], 197 [M$^+$–4CO–HNMe$_2$–(CH$_3$)$_2$CHCHO], 179 [M$^+$–4CO–PhCH$_2$–NMe$_2$], 107 [M$^+$–4CO–HNMe$_2$–PhCH$_2$–(CH$_3$)$_2$CHCHO], 91 [$C_7H_7^+$].

4.4.5. Synthesis of tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-1-(but-3-enyl-2-hydroxy-1-methyl-4-phenyl)carbene]chromium(0) (**11d** and **12d**) and (R*,R*)-tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-1-(propyl-1-methyl-2-phenyl-3-carboxaldehyde)carbene]chromium(0) (**13**)

Reaction at −78 °C *for 3 h 30 min*. Complex **6**: 109 mg (0.31 mmol, one equivalent); dry THF: 4 ml; *n*-BuLi, 1.58 M: 0.20 ml (0.32 mmol, 1.03 equivalents); cinnamaldehyde **10d**: 0.08 ml (0.64 mmol, 2.1 equivalents). Crude product: 188.5 mg; d.e. > 98%. After purification (eluent: CH_2Cl_2/ETP = 8/2), 5 mg of complex **13**, 5 mg of complex **12d**, and 95 mg of complex **11d** were obtained; d.e. after purification > 98%; yield: 63.3%; yield Michael adduct **13**: 3.6% single diastereoisomer.

Reaction at −78 °C *for 30 min*. Complex **6**: 103 mg (0.29 mmol, one equivalent); dry THF: 4 ml; *n*-BuLi, 1.54 M: 0.19 ml (0.29 mmol, one equivalent); cinnamaldehyde **10d**: 0.075 ml (0.60 mmol, two equivalents). Crude product: 179 mg; d.e.: 90%. After purification (eluent: CH_2Cl_2/ETP = 8/2) 4 mg of complex **13**, 4 mg of complex **12d**, and 114 mg of complex **11d** were obtained; d.e. after purification > 98%; yield: 80%; yield Michael adduct **13**: 3% single diastereoisomer.

Reaction at −30 °C. Complex **6**: 150 mg (0.42 mmol, one equivalent); dry THF: 4 ml; *n*-BuLi, 1.58 M: 0.27 ml (0.43 mmol, one equivalent); cinnamaldehyde **10d**: 0.11 ml (0.87 mmol, 2.1 equivalents). Crude product: 255 mg; d.e.: 18%. After purification (eluent: CH_2Cl_2/ETP = 8/2), 36 mg of complex **13**, 19 mg of complex **12d**, and 45 mg of complex **11d** were obtained; d.e. after purification: 42%; yield: 31.1%; yield Michael adduct **13**: 17.5% single diastereoisomer.

4.4.5.1. (R*,S*,E)-Tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-1-(but-3-enyl-2-hydroxy-1-methyl-4-phenyl)carbene]chromium(0) (**11d**).

Complex **11d** (major diastereoisomer): red viscous oil; Rf: 0.01 (eluent: ETP/CH_2Cl_2 = 3/7). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.5–7.0 (10H, m, H_{aromat}), 6.82 (1H, d, J = 16 Hz, CH=C*H*Ph), 6.45 (1H, dd, J_1 = 16 Hz, J_2 = 6.9 Hz, C*H*=CHPh), 4.82 (1H, d, J = 17.2 Hz, CH_2Ph), 4.8–4.6 (1H, m, HOC*H*), 4.59 (1H, d, J = 17.2 Hz, CH_2Ph), 2.87 (1H, dq, J_1 = 8 Hz, J_2 = 6.5 Hz, CrCC*H*CH$_3$), 2.76, 2.75 (6H, s, NMe$_2$), 2.06 (1H, s br., OH), 1.52 (3H, d, J = 6.5 Hz, CrCCHC*H*$_3$); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 291.4 ($C_{carbene}$), 231.7, 229.3, 219.4, 218.2 (CO), 136.2 (Cq CH=CH*Ph*), 133.4 (Cq NCH$_2$*Ph*), 132.1 (CH=*C*HPh), 129.8, 129.4, 128.6, 128.4, 127.9, 126.6, 126.0 (C Ph + *C*H=CHPh), 75.5 (CHOH), 52.6, 52.1 (NMe$_2$), 50.4 (CrC*C*H), 49.4 (N*C*H$_2$Ph), 16.3 (CrCCH*C*H$_3$); IR/FT (neat) ν (cm^{-1}): 3388 (OH), 1997 (*trans*-CO), 1865, 1807 (*cis*-CO), 752 ($\gamma CH_{arom.}$), 679 ($\delta CH_{arom.}$); MS (FAB$^+$) *m/z* 486 [M$^+$], 458 [M$^+$–CO], 430 [M$^+$–2CO], 402 [M$^+$–3CO], 374 [M$^+$–4CO], 329 [M$^+$–4CO–NHMe$_2$], 283 [M$^+$–4CO–PhCH$_2$], 238 [M$^+$–4CO–HNMe$_2$–PhCH$_2$],197 [M$^+$–4CO–NHMe$_2$–PhCH=CHCHO], 91 [$C_7H_7^+$].

4.4.5.2. (R*,R*,E)-Tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-1-(but-3-enyl-2-hydroxy-1-methyl-4-phenyl)carbene]chromium(0) (**12d**).

Complex **12d** (minor diastereoisomer): red viscous oil; Rf: 0.23 (eluent: ETP/CH_2Cl_2 = 3/7). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.5–7.2 (10H, m, H_{aromat}), 6.73 (1H, d, J = 15.8 Hz, CH=C*H*Ph), 6.18 (1H, dd, J_1 = 15.8 Hz, J_2 = 7.93 Hz, C*H*=CHPh), 5.08 (1H, d, J = 17.3 Hz, CH_2Ph), 4.8–4.6 (1H, m, HOC*H*), 4.62 (1H, d, J = 17.3 Hz, CH_2Ph), 2.89 (3H, s, NMe$_2$), 2.76 (1H, dq, J_1 = 9.1 Hz, J_2 = 6.6 Hz, CrCC*H*CH$_3$), 2.75 (3H, s, NMe$_2$), 2.14 (1H, d, J = 2.9 Hz, OH), 1.31 (3H, d, J = 6.6 Hz, CrCCHC*H*$_3$); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 292.6 ($C_{carbene}$), 232.2, 229.6, 219.1, 218.5 (CO), 136.1 (Cq CH=CH*Ph*), 133.9 (Cq NCH$_2$*Ph*), 133.6 (CH=*C*HPh), 129.4, 129.1, 128.6, 128.4, 128.0, 126.6, 126.1 (C Ph + *C*H=CHPh), 77.8 (CHOH), 52.8, 52.1 (NMe$_2$), 49.2 (N*C*H$_2$Ph), 49.0 (CrC*C*H), 16.3 (CrCCH*C*H$_3$); IR/FT (neat) ν (cm^{-1}): 3391 (OH), 1998 (*trans*-CO), 1868, 1827 (*cis*-CO), 753 ($\gamma CH_{arom.}$), 683 ($\delta CH_{arom.}$); MS (FAB$^+$) *m/z* 486 [M$^+$], 458 [M$^+$–CO], 430 [M$^+$–2CO], 402 [M$^+$–3CO], 374 [M$^+$–4CO], 329 [M$^+$–4CO–NHMe$_2$], 283 [M$^+$–4CO–PhCH$_2$], 238 [M$^+$–4CO–HNMe$_2$–PhCH$_2$],197 [M$^+$–4CO–NHMe$_2$–PhCH=CHCHO], 91 [$C_7H_7^+$].

4.4.5.3. (R*,R*)-Tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-1-(propyl-1-methyl-2-phenyl-3-carboxaldehyde)carbene]chromium(0) (**13**).

Complex **13** (from Michael addition): red viscous oil; Rf: 0.3 (eluent: ETP/CH_2Cl_2 = 3/7). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.60 (1H, m, CHO), 7.4–6.9 (10H, m, H_{aromat}), 4.17 (1H, d, J = 17.2 Hz, CH_2Ph), 4.02 (1H, d, J = 17.2 Hz, CH_2Ph), 3.80 (1H, td, J_1 = 10 Hz, J_2 = 4.8 Hz, CHC*H*Ph), 3.06 (1H, ddd, J_1 = 16.4 Hz, J_2 = 4.8 Hz, J_3 = 1 Hz, CH$_2$CO), 2.94 (1H, dq, J_1 = 10 Hz, J_2 = 6.5 Hz, CH$_3$C*H*), 2.74 (1H, ddd, J_1 = 16.4 Hz, J_2 = 10 Hz, J_3 = 3.1 Hz, CH$_2$CO), 2.60, 2.53 (6H, s, NMe$_2$), 1.49 (1H, d, J = 6.5 Hz, CH_3CH); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 293.8 ($C_{carbene}$), 232.1, 229.2, 219.8, 218.8 (CO), 201.0 (CHO), 141.9, 133.5 (Cq Ph), 129.5, 128.9, 128.5, 127.5, 125.8 (C Ph), 52.4, 51.9 (NMe$_2$), 49.0 (*C*H$_2$Ph), 48.6 (CrC*C*H), 46.5 (*C*H$_2$CO), 44.3 (*C*HPh),

18.4 (CH_3). IR/FT (neat) ν (cm^{-1}): 2728 (overtone CHO), 1997 (*trans*-CO), 1866, 1829 (*cis*-CO), 1723 (CHO), 723 ($\gamma CH_{arom.}$), MS (FAB^+) *m/z* 486 [M^+], 458 [M^+–CO], 430 [M^+–2CO], 402 [M^+–3CO], 374 [M^+–4CO], 329 [M^+–4CO–$NHMe_2$], 283 [M^+–4CO–$PhCH_2$], 239 [M^+–4CO–NMe_2–$PhCH_2$], 198 [M^+–4CO–NMe_2–PhCH=CHCHO], 91 [$C_7H_7^+$].

4.4.6. Synthesis of tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-1-(ethyl-1-methyl-2-ferrocenyl-2-hydroxy)carbene]chromium(0) (**11e** and **12e**)

Reaction at −78 °C *for 3 h 30 min*. Complex **6**: 107 mg (0.3 mmol, one equivalent); dry THF: 4 ml; *n*-BuLi, 1.54 M: 0.20 ml (0.31 mmol, one equivalent); ferrocenylaldehyde **10e**: 128 mg (0.6 mmol, two equivalents). Crude product: 243 mg; d.e.: 52%. After purification (eluent: CH_2Cl_2), 30 mg of complex **12e** and 101 mg of complex **11e** were obtained; d.e. after purification: 54%; yield: 76.7%.

Reaction at −78 °C *for 30 min*. Complex **6**: 103 mg (0.29 mmol, one equivalent); dry THF: 4 ml; *n*-BuLi, 1.54 M: 0.19 ml (0.29 mmol, one equivalent); ferrocenylaldehyde **10e**: 127 mg (0.59 mmol, two equivalents). Crude product: 236 mg; d.e.: 90%. After purification (eluent: CH_2Cl_2), 6 mg of complex **12e** and 133 mg of complex **11e** were obtained; d.e. after purification: 91%; yield: 84%.

4.4.6.1. (R*,S*)-Tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-1-(ethyl-1-methyl-2-ferrocenyl-2-hydroxy)carbene]chromium(0) (**11e**).

Complex **11e** (major diastereoisomer): orange solid; m.p. 112–113 °C (Et_2O/hexane). Anal. Calcd for $C_{27}H_{28}CrFeN_2O_5$: C, 57.06; H, 4.97; N, 4.93. Found: C, 56.92; H, 5.13; N, 4.81%. Rf: 0.29 (eluent: CH_2Cl_2). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.4–6.85 (5H, m, H_{aromat}), 4.62 (1H, d br., $J = 8.9$ Hz, OHC*H*Cp), 4.3–4.15 (10H, m, Cp+CH_2Ph), 4.03 (1H, d, $J = 17.3$ Hz, CH_2Ph), 2.69 (1H, dq, $J_1 = 8.9$ Hz, $J_2 = 6.3$ Hz, CrCC*H*CH_3), 2.68, 2.58 (6H, s, NMe_2), 2.36 (1H, d, $J = 1.2$ Hz, OH), 1.63 (3H, d, $J = 6.3$ Hz, CrCCHCH_3); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 291.8 ($C_{carbene}$), 231.8, 229.5, 220.3, 218.4 (CO), 133.7 (Cq NCH_2Ph), 129.4, 128.3, 125.7 (C Ph), 93.6 (Cq Cp), 70.9 (CHOH), 68.8, 68.6, 68.0, 64.3 (Cp), 52.5 (NMe_2), 52.1 (CrC*C*H), 49.1 (N*C*H_2Ph), 17.9 (CrCCH*C*H_3); IR/FT (neat) ν (cm^{-1}): 3565 (OH), 1996 (*trans*-CO), 1866, 1833 (*cis*-CO), 736 ($\gamma CH_{arom.}$), 685 ($\delta CH_{arom.}$).

4.4.6.2. (R*,R*)-Tetracarbonyl[(N-benzyl-N′,N′-dimethylhydrazinyl)-1-(ethyl-1-methyl-2-ferrocenyl-2-hydroxy)carbene]chromium(0) (**12e**).

Complex **12e** (minor diastereoisomer): orange solid; m.p. 125–126 °C (Et_2O/hexane). Anal. Calcd for $C_{27}H_{28}CrFeN_2O_5$: C, 57.06; H, 4.97; N, 4.93. Found: C, 56.90; H, 5.15; N, 4.87%. Rf: 0.47 (eluent: CH_2Cl_2). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.5–7.1 (5H, m, H_{aromat}), 5.12 (1H, d, $J = 17.3$ Hz, CH_2Ph), 4.67 (1H, d, $J = 9.1$ Hz, OHC*H*Cp), 4.54 (1H, d, $J = 17.3$ Hz, CH_2Ph), 4.4–4.1 (9H, m, Cp), 2.94, 2.71 (6H, s, NMe_2), 2.57 (1H, dq, $J_1 = 9.1$ Hz, $J_2 = 6.5$ Hz, CrCC*H*CH_3), 2.32 (1H, d, $J = 1.3$ Hz, OH), 1.14 (3H, d, $J = 6.5$ Hz, CrCCHCH_3); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 292.5 ($C_{carbene}$), 232.5, 229.8, 218.9, 218.7 (CO), 134.2 (Cq NCH_2Ph), 129.4, 128.3, 126.0 (C Ph), 94.1 (Cq Cp), 74.4 (CHOH), 69.7, 68.4, 68.1, 64.2 (Cp), 52.6, 52.1 (NMe_2), 50.8 (CrC*C*H), 49.1 (N*C*H_2Ph), 16.3 (CrCCH*C*H_3); IR/FT (neat) ν (cm^{-1}): 3584 (OH), 1997 (*trans*-CO), 1869, 1827 (*cis*-CO), 730 ($\gamma CH_{arom.}$), 681 ($\delta CH_{arom.}$).

4.5. Oxidations

We used general procedures previously published [13] for the oxidation of hydrazinocarbene complexes.

4.5.1. Synthesis of (R*,R*)-2-(3-oxo-cyclohexyl)-propionic acid N-benzyl-N′,N′-dimethyl-hydrazide (**13b**)

Hydrazinocarbene complex **9b**: 107 mg (0.24 mmol, one equivalent); K_2HPO_4: 422 mg (2.4 mmol, 10 equivalents); KH_2PO_4: 329 g (2.4 mmol, 10 equivalents); TBAB: 4.7 mg (0.01 mmol, 4.2 mol%); $Ca(OCl)_2$: 78 mg (0.35 mmol, 1.4 equivalents); water: 5 ml; AcOEt: 5 ml; after work-up, 66 mg of the hydrazide **13b** was obtained; yield 92%.

4.5.2. (R*,R*)-2-(3-Oxo-cyclohexyl)-propionic acid N-benzyl-N′,N′-dimethyl-hydrazide (**13b**)

Complex **13b**: colourless oil. Rf: 0.71 (eluent: MTBE). HRMS (EI) for $C_{18}H_{26}N_2O_2$: [M^+] calc.: 302.19943, found: 302.1977; [$M+1^+$] calc.: 303.20725, found: 303.2063. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.5–7.1 (5H, m, $CH_{arom.}$), 4.65 (1H, d, $J = 15.8$ Hz, CH_2Ph), 4.59 (1H, d, $J = 15.8$ Hz, CH_2Ph), 3.5–3.3 (1H, m, C*H*Me), 2.49 (6H, s, NMe_2), 2.6–1.3 (9H, m, cycloesanone), 1.10 (3H, d, $J = 6.6$ Hz, CrCCHCH_3); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 211.6 (CO ketone), 178.2 (CO hydrazide), 139.4 (C_q Ph), 128.4, 127.4, 126.8 (C Ph), 45.1 (CH*C*H_2CO), 44.8 (NMe_2), 41.4 (CH_2CH_2CO), 41.3 (*C*HCON), 39.8 (*C*HCH_2CO), 29.8 (CH_2CH_2CO), 25.0 (CH*C*H_2CH_2), 15.4 (CH_3). IR/FT (neat) ν (cm^{-1}): 1708 (νC=O ketone), 1650 (νC=O hydrazide), 1496 (arC–C), 1350 (δsy CH_3), 730 ($\gamma CH_{arom.}$), 699 ($\delta CH_{arom.}$). MS (EI) *m/z* 303 [M^++1], 302 [M^+], 259 [M^++1–NMe_2], 211 [M^+–$PhCH_2$], 150 [M^++1–COR], 149 [M^+–COR], 106 [M^++1–COR–NMe_2], 91 [$C_7H_7^+$], 79 [$C_6H_7^+$], 77 [$C_6H_5^+$], 65 [$C_5H_5^+$].

4.5.3. Synthesis of (R,R*)-2-methyl-5-oxo-3,5-diphenyl-pentanoic acid N-benzyl-N′,N′-dimethyl-hydrazide (**13c**)*

Hydrazinocarbene complex **9c**: 204 mg (0.36 mmol, one equivalent); K_2HPO_4: 635 mg (3.6 mmol, 10 equivalents); KH_2PO_4: 496 mg (3.6 mmol, 10 equivalents); TBAB: 7 mg (0.015 mmol, 4.2 mol%); $Ca(OCl)_2$: 202 mg (0.92 mmol, 2.5 equivalents); water: 10 ml; AcOEt: 10 ml; after work-up, 145 mg of hydrazide **13c** was obtained; yield 96.5%.

4.5.4. (R,R*)-2-Methyl-5-oxo-3,5-diphenyl-pentanoic acid N-benzyl-N′,N′-dimethyl-hydrazide (**13c**)*

Complex **13c**: white solid, m.p. 144 °C (Et_2O/hexane). Anal. Calcd for $C_{27}H_{30}N_2O_2$: C, 78.23; H, 7.29; N, 6.76. Found: C, 78.44; H, 7.51; N, 6.46%. Rf: 0.75 (eluent: MTBE). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.87 (2H, d, $J = 7.4$ Hz, $COPh_{arom.\ ortho}$), 7.6–6.7 (13H, m, $CH_{arom.}$), 4.74 (1H, d, $J = 15.9$ Hz, CH_2Ph), 4.27 (1H, d, $J = 15.9$ Hz, CH_2Ph), 4.15–4.0 (1H, m, C*H*Ph), 3.95–3.8 (1H, m, C*H*Me), 3.6–3.3 (2H, m, CH_2CO), 2.54 (3H, s, NMe_2), 2.26 (3H, s, NMe_2), 1.28 (3H, d, $J = 6.3$ Hz, CH*Me*); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 199.0 (*C*OPh), 177.5 (CO), 143.5, 138.9, 137.3 (C_q Ph), 133–126 (C Ph), 44.9, 44.5 (NMe_2), 43.8 (*C*HPh), 41.3 (N*C*H_2Ph), 1.0 (*C*H_2CO), 40.5 (*C*HCON), 15.5 (NCOCH*C*H_3). IR/FT (neat) ν (cm^{-1}): 1686 (νC=O ketone), 1650 (νC=O hydrazide), 1495 (arC–C), 1353 (δsy CH_3), 740 ($\gamma CH_{arom.}$), 703 ($\delta CH_{arom.}$).

4.5.5. Synthesis of (R,S*)-3-hydroxy-2,4-dimethyl-pentanoic acid N-benzyl-N′,N′-dimethyl-hydrazide (**14c**)*

Hydrazinocarbene complex **11c**: 249 mg (0.58 mmol, one equivalent); KH_2PO_4: 797 mg (5.8 mmol, 10 equivalents); $NaBO_3 \cdot 4H_2O$: 459 mg (2.98 mmol, five equivalents); KI: 0.17 ml (0.1 M, 0.017 mmol, 3 mol%); water: 16 ml; AcOEt: 16 ml; 144 mg of hydrazide **14c** was obtained; yield 88.9%.

4.5.6. (R,S*)-3-Hydroxy-2,4-dimethyl-pentanoic acid N-benzyl-N′,N′-dimethyl-hydrazide (**14c**)*

Complex **14c**: colourless oil. Rf: 0.1 (eluent: CH_2Cl_2). HRMS (EI) for $C_{16}H_{26}N_2O_2$: [M^+] calc.: 278.19943, found: 278.1989. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.4–7.1 (5H, m, C–H aromatic), 4.66 (1H, d, $J = 16$ Hz, CH_2Ph), 4.59 (1H, d, $J = 16$ Hz, CH_2Ph), 3.66 (1H, dq, $J_{Me-CHCON} = 7.3$ Hz, $J_{CH-CHOH} = 2.2$ Hz, C*H*Me), 3.41 (1H, dd, $J_{CH-CHMe_2} = 8.8$ Hz, $J_{CH-CHO} = 2.2$ Hz, C*H*OH), 2.8–2.2 (1H, s very broad, OH), 2.51 (3H, s, NMe_2), 2.48 (3H, s, NMe_2), 1.82–1.65 (1H, m, C*H*Me_2), 1.16 (3H, d, $J_{Me-CHCON} = 7.3$ Hz, *Me*CHCON), 1.05 (3H, d, $J_{Me_2CH} = 6.6$ Hz, *Me*$_2$CH), 0.87 (3H, d, $J_{Me_2CH} = 7$ Hz, *Me*$_2$CH); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 180.5 (CO), 138.7 (C_q NCH_2Ph), 128.4, 126.9, 126.6 (C Ph), 77.3 (COH), 44.6 (NMe_2), 41.1 (N*C*H_2Ph), 35.4 (*C*HCON), 30.3 (*C*HMe_2), 19.3, 18.8 (CH*Me*$_2$), 10.1 (NCOCH*C*H_3). IR/FT (neat) ν (cm^{-1}): 3446 (νOH), 1631 (νC=O), 1497 (arC–C), 1353 (δsy CH_3), 729 ($\gamma CH_{arom.}$), 700 ($\delta CH_{arom.}$). MS (EI) *m/z* 279 [$M^+ + 1$], 278 [M^+], 235 [$M^+ + 1 - NMe_2$], 217 [$M^+ + 1 - NMe_2 - H_2O$], 187 [$M^+ - PhCH_2$], 150 [$M^+ + 1 - COCHMeCOHCHMe_2$], 149 [100%, $M^+ - COCHMeCOHCHMe_2$], 106 [$M^+ + 1 - COCHMeCOHCHMe_2 - NMe_2$], 91 [$C_7H_7^+$], 79 [$C_6H_7^+$], 77 [$C_6H_5^+$], 65 [$C_5H_5^+$].

4.5.7. Synthesis of (R,R*)-3-hydroxy-2,4-dimethyl-pentanoic acid N-benzyl-N′,N′-dimethyl-hydrazide (**15c**)*

Hydrazinocarbene complex **12c**: 129 mg (0.30 mmol, one equivalent); KH_2PO_4: 415 mg (3.05 mmol, 10.1 equivalents); $NaBO_3 \cdot 4H_2O$: 239 mg + 82 mg after 1 h 30 min (2.08 mmol, 5 + 1.8 equivalents); KI: 0.09 ml (0.1 M, 0.009 mmol, 3 mol%); water: 10 ml; AcOEt: 10 ml; 78 mg of hydrazide **15c** was obtained; yield 92%.

4.5.8. (R,R*)-3-Hydroxy-2,4-dimethyl-pentanoic acid N-benzyl-N′,N′-dimethyl-hydrazide (**15c**)*

Complex **15c**: colourless oil. Rf: 0.04 (eluent: CH_2Cl_2). HRMS (EI) for $C_{16}H_{26}N_2O_2$: [M^+] calc.: 278.19943, found: 278.1991. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.4–7.1 (5H, m, C–$H_{arom.}$), 4.65 (1H, d, $J = 16.2$, CH_2Ph), 4.59 (1H, d, $J = 16.2$, CH_2Ph), 3.70 (1H, dq, $J_{Me-CHCON} = 7$ Hz, $J_{CH-CHOH} = 4.4$ Hz, C*H*Me), 3.25 (1H, dd, $J_{CH-CHMe_2} = 7$ Hz, $J_{CH-CHO} = 4.4$ Hz, C*H*OH), 2.53 (3H, s, NMe_2), 2.51 (3H, s, NMe_2), 1.8–1.5 (1H, s broad, OH), 1.8–1.6 (1H, m, C*H*Me_2), 1.29 (3H, d, $J_{Me-CHCON} = 7$ Hz, *Me*CHCON), 1.00 (3H, d, $J_{Me_2CH} = 6.7$ Hz, *Me*$_2$CH), 0.93 (3H, d, $J_{Me_2CH} = 7$ Hz, *Me*$_2$CH); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 179.9 (CO), 138.9 (C_q NCH_2Ph), 128.4, 127.3, 126.8 (C Ph), 80.1 (COH), 44.9, 44.8 (NMe_2), 41.2 (N*C*H_2Ph), 36.3 (*C*HCON), 32.3 (*C*HMe_2), 19.8, 18.2 (CH*Me*$_2$), 16.35 (NCOCH*C*H_3). IR/FT (neat) ν (cm^{-1}): 3430 (νOH), 1626 (νC=O), 1497 (arC–C), 1353 (δsy CH_3), 727($\gamma CH_{arom.}$), 700 ($\delta CH_{arom.}$). MS (EI) *m/z* 279 [$M^+ + 1$], 278 [M^+], 235 [$M^+ + 1 - NMe_2$], 217 [$M^+ + 1 - NMe_2 - H_2O$], 187 [$M^+ - PhCH_2$], 150 [$M^+ + 1 - COCHMeCOHCHMe_2$], 149 [100%, $M^+ - COCHMeCOHCHMe_2$], 106 [$M^+ + 1 - COCHMeCOHCHMe_2 - NMe_2$], 91 [$C_7H_7^+$], 79 [$C_6H_7^+$], 77 [$C_6H_5^+$], 65 [$C_5H_5^+$].

4.5.9. Synthesis of (R,S*)-3-hydroxy-2-methyl-pentanoic acid N-benzyl-N′,N′-dimethyl-hydrazide (**14b**)*

Hydrazinocarbene complex **11b**: 309 mg (0.75 mmol, one equivalent); KH_2PO_4: 1.024 g (7.53 mmol, 10.1 equivalents); $NaBO_3 \cdot 4H_2O$: 591 mg + 199 mg after 1 h 30 min (5.1 mmol, 5 + 1.8 equivalents); KI: 0.22 ml (0.1 M, 0.022 mmol, 3 mol%); water: 20 ml; AcOEt: 20 ml; 184 mg of hydrazide **14b** was obtained; yield 93%.

4.5.10. (R,S*)-3-Hydroxy-2-methyl-pentanoic acid N-benzyl-N′,N′-dimethyl-hydrazide (**14b**)*

Complex **14b**: colourless oil. Rf: 0.12 (eluent: CH_2Cl_2). HRMS (EI) for $C_{15}H_{24}N_2O_2$: [M^+] calc.: 264.18378, found: 264.1831; [$M+1^+$] calc.: 265.19160, found: 264.1920. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.4–7.1 (5H, m, $CH_{arom.}$), 4.66 (2H, d, $J=15.8$, CH_2Ph), 4.58 (2H, d, $J=15.8$, CH_2Ph), 4.21 (1H, s broad, OH), 3.78 (1H, ddd, $J_{CHOH-CH_2}=5.5$ Hz, $J_{CHOH-CH_2}=7.7$ Hz, $J_{CMeH-CHOH}=2.2$ Hz, C*H*OH), 3.42 (1H, dq, $J_{Me-CHCON}=7.0$ Hz, $J_{CH-CHOH}=2.2$ Hz, C*H*CH_3), 2.51 (3H, s, NMe_2), 2.48 (3H, s, NMe_2), 1.7–1.51 (1H, m, CH_2CH_3), 1.51–1.30 (1H, m, CH_2CH_3), 1.18 (3H, d, $J_{Me-CHCON}=7.0$ Hz, CHCH_3), 0.98 (3H, t, $J_{CH_2-CH_3}=7.5$, CH_2CH_3). ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 180.3 (CO), 138.6 (C_q NCH_2*Ph*), 128.3, 126.8, 126.7 (C Ph), 73.1 (COH), 44.5 (NMe_2), 41.0 (N*C*H_2Ph), 37.8 (*C*HCON), 26.5 (*C*H_2CH_3), 10.2 (NCOCH*C*H_3; CH_2*C*H_3). IR/FT (neat) ν (cm^{-1}): 3436 (νOH), 1630 (νC=O), 1497 (arC–C), 1353 (δsy CH_3), 730 ($\gamma CH_{arom.}$), 700 ($\delta CH_{arom.}$). MS (EI) *m/z* 265 [$M^+ +1$], 264 [M^+], 221 [$M^+ +1-NMe_2$], 203 [$M^+ +1-NMe_2-H_2O$], 173 [$M^+ -PhCH_2$], 150 [$M^+ +1-$COCHMeCOHEt], 149 [100%, $M^+ -$COCHMeCOHEt], 92 [$M^+ +1-$COCHMeCOHEt$-NMe_2$], 91 [$C_7H_7^+$], 79 [$C_6H_7^+$], 77 [$C_6H_5^+$], 65 [$C_5H_5^+$].

4.5.11. Synthesis of (R,R*)-3-hydroxy-2-methyl-pentanoic acid N-benzyl-N′,N′-dimethyl-hydrazide (**15b**)*

Hydrazinocarbene complex **12b**: 144 mg (0.35 mmol, one equivalent); KH_2PO_4: 480 mg (3.53 mmol, 10.1 equivalents); $NaBO_3 \cdot 4H_2O$: 276 mg+96 mg after 1 h 30 min (2.4 mmol, 5+1.8 equivalents); KI: 0.11 ml (0.1 M, 0.01 mmol, 3.1 mol%); water: 10 ml; AcOEt: 10 ml; 90 mg of hydrazide **15b** was obtained; yield 97.6%.

4.5.12. (R,R*)-3-Hydroxy-2-methyl-pentanoic acid N-benzyl-N′,N′-dimethyl-hydrazide (**15b**)*

Complex **15b**: colourless oil. Rf: 0.04 (eluent: CH_2Cl_2). HRMS (EI) for $C_{15}H_{24}N_2O_2$: [M^+] calc.: 264.18378, found: 264.1829. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.4–7.1 (5H, m, $CH_{arom.}$), 4.62 (2H, s, CH_2Ph), 3.84 (1H, s, OH), 3.6–3.4 (2H, m, C*H*MeC*H*OH), 2.52 (3H, s, NMe_2), 2.49 (3H, s, NMe_2), 1.6–1.4 (2H, m, CH_2CH_3), 1.27 (3H, d, $J_{Me-CHCON}=7.0$ Hz, CHCH_3), 1.00 (3H, t, $J_{CH_2-CH_3}=7.4$, CH_2CH_3). ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 179.6 (CO), 138.8 (C_q NCH_2*Ph*), 128.7, 127.0, 126.8 (C Ph), 76.0 (COH), 44.8 (NMe_2), 41.2 (N*C*H_2Ph), 39.1 (*C*HCON), 29.6 (*C*H_2CH_3), 15.9 (NCOCH*C*H_3), 10.5 (CH_2*C*H_3). IR/FT (neat) ν (cm^{-1}): 3436 (νOH), 1630 (νC=O), 1497 (arC–C), 1353 (δsy CH_3), 728 ($\gamma CH_{arom.}$), 699 ($\delta CH_{arom.}$). MS (EI) *m/z* 265 [$M^+ +1$], 264 [M^+], 221 [$M^+ +1-NMe_2$], 203 [$M^+ +1-NMe_2-H_2O$], 173 [$M^+ -PhCH_2$], 150 [$M^+ +1-$COCHMeCOHEt], 149 [100%, $M^+ -$COCHMeCOHEt], 92 [$M^+ +1-$COCHMeCOHEt$-NMe_2$], 91 [$C_7H_7^+$], 79 [$C_6H_7^+$], 77 [$C_6H_5^+$], 65 [$C_5H_5^+$].

4.5.13. Synthesis of (R,S*)-3-hydroxy-2-methyl-phenyl-pent-4-enoic acid N-benzyl-N′,N′-dimethyl-hydrazide (**14d**)*

Hydrazinocarbene complex **11d**: 100 mg (0.20 mmol, one equivalent); KH_2PO_4: 287 mg (2.10 mmol, 10.2 equivalents); $NaBO_3 \cdot 4H_2O$: 157 mg (1.02 mmol, five equivalents); KI: 0.065 ml (0.1 M, 0.0065 mmol, 3.1 mol%); water: 6 ml; AcOEt: 6 ml; 58 mg of hydrazide **14d** was obtained; yield 84%.

4.5.14. (R,S*)-3-Hydroxy-2-methyl-phenyl-pent-4-enoic acid N-benzyl-N′,N′-dimethyl-hydrazide (**14d**)*

Complex **14d**: colourless oil. Rf: 0.5 (eluent: MTBE). HRMS (EI) for $C_{21}H_{26}N_2O_2$: [M^+] calc.: 338.1994, found: 338.1989. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.5–7.1 (10H, m, $CH_{arom.}$), 6.73 (1H, dd, $J_{allylic}=1.5$ Hz, $J_{trans}=16.2$ Hz, CH=C*H*Ph), 6.23 (1H, dd, $J_{CHOH-CHCH}=5.2$ Hz, $J_{trans}=16.2$ Hz, C*H*=CHPh), 4.66 (1H, ddd, $J_{CHOH-CHCH}=5.2$ Hz, $J_{CMeH-CHOH}=2.9$ Hz, $J_{allylic}=1.5$ Hz, C*H*OH), 4.67 (2H, d, $J=15.8$, CH_2Ph), 4.61 (2H, d, $J=15.8$, CH_2Ph), 3.57 (1H, dq, $J_{Me-CHCON}=7.0$ Hz, $J_{CMeH-CHOH}=2.9$ Hz, C*H*CH_3), 3.5–3.1 (1H, s very broad, OH), 2.53 (3H, s, NMe_2), 2.49 (3H, s, NMe_2), 1.25 (3H, d, $J_{Me-CHCON}=7.0$ Hz, CHCH_3). ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 179.6 (CO), 138.7, 137.0 (C_q Ph), 130.6, 129.7, 128.6, 128.5, 127.4, 127.0, 126.4 (C Ph+*C*H=*C*HPh), 72.7 (COH), 44.8 (NMe_2), 41.3 (N*C*H_2Ph), 39.9 (*C*HCON), 11.3 (NCOCH*C*H_3). IR/FT (neat) ν (cm^{-1}): 3410 (νOH), 1954, 1889, 1810, 1733 (overtone arom.), 1631 (νC=O and C=C), 1495 (arC–C), 1353 (δsy CH_3), 970 (δoop=CH alkenyl group), 741 ($\gamma CH_{arom.}$), 696 ($\delta CH_{arom.}$). MS (EI) *m/z* 338 [M^+], 294 [$M^+ -NMe_2$], 247 [$M^+ -PhCH_2$], 150 [$M^+ +1-$COCHMeCOHCH=CHPh], 149 [100%, $M^+ -$COCHMeCOHCH=CHPh], 131 [PhCH=CHCO$^+$], 106 [$M^+ +1-$COCHMeCOHCH=CHPh$-NMe_2$], 91 [$C_7H_7^+$], 79 [$C_6H_7^+$], 77 [$C_6H_5^+$], 65 [$C_5H_5^+$].

4.5.15. Synthesis of (R,S*)-3-ferrocenyl-3-hydroxy-2-methyl-propionic acid N-benzyl-N′,N′-dimethyl-hydrazide (**14e**)*

Hydrazinocarbene complex **11e**: 123 mg (0.21 mmol, one equivalent); KH_2PO_4: 297 mg (2.18 mmol, 10.4 equivalents); $NaBO_3 \cdot 4H_2O$: 161.5 mg (1.05 mmol, five equivalents); KI: 0.065 ml (0.1 M, 0.0065 mmol, 3.1 mol%); water: 7 ml; AcOEt: 7 ml; 80 mg of hydrazide **14e** was obtained; yield 88.1%.

4.5.16. (R,S*)-3-Ferrocenyl-3-hydroxy-2-methyl-propionic acid N-benzyl-N′,N′-dimethyl-hydrazide (**14e**)*

Complex **14e**: yellow oil; Rf: 0.5 (eluent: MTBE). HRMS (EI) for $C_{23}H_{28}FeN_2O_2$: [M^+] calc.: 420.1500,

Table 7
Crystal data and structure refinement for compounds **9b**, **9c**, **11e** and **12e**

	9b	**9c**	**11e**	**12e**
Formula	$C_{22}H_{26}CrN_2O_5$	$C_{31}H_{30}CrN_2O_5$	$C_{27}H_{28}CrFeN_2O_5$	$C_{27}H_{28}CrFeN_2O_5$
Fw	450.45	562.57	568.36	568.36
Wavelength (Å)	1.54184 (Cu–K_α)	0.71073 (Mo–K_α)	1.54184 (Cu–K_α)	0.71073 (Mo–K_α)
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions				
a (Å)	8.509(4)	18.702(5)	16.183(4)	12.033(4)
b (Å)	21.922 (5)	13.677(4)	12.236(3)	12.393(3)
c (Å)	12.470(4)	12.215(4)	13.533(5)	10.630(5)
α (°)		75.58(3)		114.55(4)
β (°)	93.85(2)	87.49(3)	93.58(5)	110.01(3)
γ (°)		71.84(3)		96.19(3)
V (Å^3)	2321(1)	2873(1)	2674(1)	1296(1)
Z, density (calc.) (Mg m^{-3})	4, 1.289	4, 1.300	4, 1.412	2, 1.457
Abs. coefficient (cm^{-1})	43.37	4.39	9.87	10.19
Max. and min. transmission factor	1.000, 0.522	1.000, 0.369	Smart	1.000, 0.727
F(0 0 0)	944	1176	1176	588
Crystal size (mm^3)	0.18 × 0.32 × 0.37	0.22 × 0.21 × 0.22	0.12 × 0.12 × 0.17	0.22 × 0.13 × 0.22
θ range (°)	4.03–69.96	3.08–28.00	1.26–27.32	3.03–28.02
Reflns. collct., independent reflections	4590, 4393	13 827, 13 827	7330, 7330	6245, 6245
Observed reflections [$I > 2\sigma(I)$]	2825	4489	3453	4629
Data/restr./param.	4393/0/282	13827/0/712	7330/0/305	6245/0/335
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0792$, $wR_2 = 0.2106$	$R_1 = 0.0832$, $wR_2 = 0.1981$	$R_1 = 0.1105$, $wR_2 = 0.2700$	$R_1 = 0.0534$, $wR_2 = 0.1262$
R indices (all data)	$R_1 = 0.1077$, $wR_2 = 0.2339$	$R_1 = 0.2116$, $wR_2 = 0.2543$	$R_1 = 0.1939$, $wR_2 = 0.3602$	$R_1 = 0.0768$, $wR_2 = 0.1401$

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_c^2-F_o^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

found: 420.1512. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.4–7.0 (5H, m, H_{aromat}), 4.69 (1H, d br., $J = 5.8$ Hz, OHC*H*Cp), 4.59 (1H, d, $J = 15.8$ Hz, CH_2Ph), 4.50 (1H, d, $J = 15.8$ Hz, CH_2Ph), 4.4–4.05 (8H, m, Cp), 3.52 (1H, dq, $J_1 = 5.8$ Hz, $J_2 = 6.9$ Hz, CrCC*H*CH$_3$), 3.48 (1H, s broad, Cp), 2.44 (3H, s, NMe_2), 2.27 (3H, s, NMe_2), 1.71 (1H, s broad, OH), 1.20 (3H, d, $J = 6.9$ Hz, CrCCHC*H*$_3$); ^{13}C-NMR DEPT ($CDCl_3$, 75 MHz) δ (ppm): 178.8 (CO), 138.8 (Cq NCH$_2$*Ph*), 128.3, 127.3, 126.8 (C Ph), 91.7 (Cq Cp), 71.3 (CHOH), 68.5, 67.9, 67.4, 65.6 (Cp), 44.7, 44.6 (NMe_2), 42.5 (*C*HCON), 41.2 (N*C*H$_2$Ph), 13.0 (COCH*C*H$_3$); IR/FT (neat) ν (cm^{-1}): 3459 (νOH), 1627 (νC=O), 1496 (arC–C), 1352 (δsy CH$_3$), 736 (γCH$_{arom.}$), 701 (δCH$_{arom.}$). MS (EI) *m*/*z* 421 [M$^+$ + 1], 420 [M$^+$], 375 [M$^+$–HNMe_2], 329 [M$^+$-PhCH$_2$], 149 [M$^+$–COCHMeCOHFeCp$_2$], 149 [100%, M$^+$–COCHMeCOHEt], 92 [M$^+$ + 1–COCHMeCOHEt–NMe_2], 91 [$C_7H_7^+$], 79 [$C_6H_7^+$], 77 [$C_6H_5^+$], 65 [$C_5H_5^+$].

4.5.17. X-ray data collection, structure solution and refinement for compounds *9b*, *9c*, *11e* and *12e*

The intensity data of compounds **9b**, **9c**, **11e** and **12e** were collected at room temperature on an ENRAF Nonius CAD 4 (**9b**), Philips PW 1100 (**9c** and **12e**) and a Bruker Smart 1000 (**11e**) single-crystal diffractometers, respectively. Crystallographic and experimental details for the structures are summarised in Table 7.

The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) [25] with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms except for the carbon atoms of the phenyl ring in **11e**. When necessary, the data correction for the absorption was applied [26]. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms. In the final cycles of refinement, a weighting scheme $w = 1/[\sigma^2F_o^2+(0.1656P)^2]$ (**9b**), $w = 1/[\sigma^2F_o^2+(0.1277P)^2]$ (**9c**), $w = 1/[\sigma^2F_o^2+(0.2000P)^2]$ (**11e**), $w = 1/[\sigma^2F_o^2+(0.0666)^2+1.1617P]$ (**12e**), where $P = (F_o^2+2F_c^2)/3$ was used.

5. Supplementary material

The supplementary material for the structures includes lists of atomic coordinates for the non-H atoms, of calculated coordinates for the hydrogen atoms, of anisotropic thermal parameters and complete lists of bond lengths and angles. The details of the crystal structure investigations are deposited to the Cambridge

Crystallographic Data Centre as supplementary publications Nos. CCDC-209491 (**9b**), CCDC-209492 (**9c**), CCDC-209490 (**11e**), CCDC-209493 (**12e**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

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