The Anion of the Pentacarbonyl[(*trans*-2,6-dimethylmorpholino)-(methyl)carbene]chromium Complex in the Reactions with Nitroalkenes

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The diastereoselective Michael addition of the title anion to α-hydrogen- and α-methyl-substituted conjugated nitroalkenes leads to new γ-nitrocarbene complexes and γ-hydroximoamides, respectively. The γ-nitrocarbene complexes can be quantitatively oxidized to γ-nitrobutyric acid derivatives (precursors of GABA derivatives); the γ-hydroximoamides are formed as a result of an unexpected intramolecular transfer of an oxygen atom from the nitro group to the carbene atom, with elimination of the pentacarbonylchromium(0) group, which is recovered in high yield as the $PyCr(CO)_5$ complex.

The synthetic potential of Fischer-type carbene complexes in the formation of new carbon−carbon bonds is well documented by a host of publications[1]. A widely used general synthetic strategy involves the generation of the carbanion α to the carbene carbon atom, and its subsequent reaction with electrophilic reagents[1a][1d][1e].

Anions of chiral amino carbene complexes have recently been successfully used in Michael 1,4-addition reactions to enones affording δ-oxo carbene complexes with good to high levels of diastereoselectivity[2]. In particular, we showed that the incorporation of *trans*-2,6-dimethylmorpholine as a C_2-symmetric chiral auxiliary in the carbene structure not only leads to stereoselective formation of carbon−carbon bonds, despite the fact that the stereogenic centers are far from the reaction site, but also made possible to determinate the diastereomeric excesses directly from the ^{1}H-NMR spectra of the crude reaction mixtures[2b][3].

As a continuation of our work[2b][3] and with the aim of examining the scope of the use of C_2-symmetric amine-substituted Fischer carbene α-anions in stereoselective carbon−carbon bond formation, we have extended our studies to include the addition reaction to nitroalkenes, which are powerful Michael acceptors and readily react with a number of nucleophiles[5]. However, a problem associated with the use of nitroalkenes in reactions with carbon-centered nucleophiles is their propensity to undergo polymerization, which reduces the chemical yields and leads to complicated product mixtures. To overcome these drawbacks, alternative methods have appeared in the literature which employ acidic instead of basic conditions[6], or very low temperatures and the addition of hexamethylphosphoric acid triamide[7]. No examples of the addition of Fischer carbene anions to nitroalkenes have hitherto been reported. Due to the effective delocalization of the negative charge into the $Cr(CO)_5$ group, the anions of Fischer amino carbene complexes are well-stabilized and are soft nucleophiles. However, at the same time they exhibit high reactivity in aldol additions[1d][8], alkylation reactions[1d], and 1,4-conjugate additions[2], even under very mild conditions. For these reasons they could, in principle, be good candidates for conjugate addition to nitro olefins. Moreover, the incorporation of a nitro group into a carbene complex structure offers various interesting possibilities, since the nitro group can, in turn, be transformed into a variety of different functionalities[9].

In this paper, we report the results of diastereoselective additions of the chiral racemic morpholino-substituted carbene complex **1** to two different series of (*E*)-2-aryl-nitroalkenes: compounds **2a−d**, in which a hydrogen atom is attached to the carbon atom bearing the nitro group; and compounds **3a−c**, in which a methyl group is attached to this carbon atom. We will show that the nature of the products depends on the structure of the nitroalkene employed. In addition, we will show that the γ-nitro carbene complex **4b** can be cleaved to give the corresponding β-aryl-γ-nitrobutyric acid amide, showing that complexes **4a−d** are potential precursors of γ-aminobutyric acids, an important class of biologically active compounds[10].

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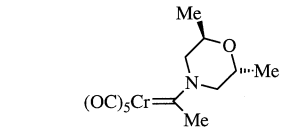

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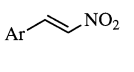
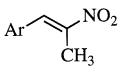


2a-d



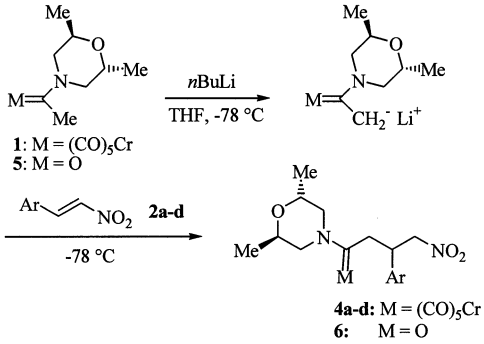
3a-c

2	Ar
a :	Ph
b :	*p*-Cl-Ph
c :	2-furyl
d :	2-thienyl

3	Ar
a :	Ph
b :	2-furyl
c :	2-thienyl

The reactions of **1** with **2a–d** are shown in Scheme 1 (see Experimental Section, Procedure A). The conjugate base of **1** was generated with *n*BuLi at −78°C and the nitroalkene was added at the same temperature. The expected 1,4-addition products **4a–d** were obtained in the chemical yields and with the diastereoselectivities indicated in Scheme 1. The high chemical yields reflect the expected good reactivity of the anion of complex **1** with nitroalkenes at −78°C. In no case was the formation of by-products arising from polymerization of the Michael acceptor observed.

Scheme 1



Entry	product	Ar	yield%	d.e.%
1	**4a**	Ph	86	30
2	**4b**	*p*-ClPh	80	50
3	**4b**	*p*-ClPh	66[a]	80[a]
4	**4c**	2-furyl	91	40
5	**4d**	2-thienyl	91	20
6	**6**	*p*-ClPh	50[b]	6[b]

[a] Reaction performed at −108°C. − [b] The use of LDA gave 77% yield and 5% d.e.

Diastereoselectivities were determined from the ^{1}H-NMR spectra of the crude reaction mixtures and, in some cases, were confirmed with the aid of ^{13}C-NMR spectra. The d.e. values were not particularly high for the reactions performed at −78°C, but we consider them particularly interesting and satisfactory in view of the fact that the inducing centers are five atoms away from the newly formed stereogenic center. In addition, we found that d.e. values were significantly higher than those obtained by treating the anion of *N*-acetylmorpholine (**5**)[11] (the organic isolobal analogue of complex **1**) with *p*-chloro-β-nitrostyrene (**2b**) (Scheme 1, entry 6). In this case, the amide enolate was generated with both, *n*BuLi and LDA at −78°C[11] (see Procedure D). Chemical yields were lower than those obtained with the carbene complex **1**, and d.e. values were very low. These results indicate that the $Cr(CO)_5$ moiety, coupled with the presence of the stereogenic unit *trans*-2,6-dimethylmorpholine, has a marked effect both on the reactivity of the anion of **1** and on the stereochemical outcome of the reactions in Scheme 1 (entries 1−5). A significant improvement of the d.e. (from 47 to 80%) was achieved by performing the reaction of **1** with *p*-chloro-β-nitrostyrene (**2b**) at −108°C (entry 3, Scheme 1); the chemical yield was slightly lower (66 instead of 80%), and 26% of unreacted starting complex **1** was recovered. All reaction mixtures could be purified by means of column chromatography and the two diastereoisomers formed in each reaction were obtained as pure complexes. The mixture of the two diastereoisomers **4b** (entry 2, Scheme 1) was quantitatively oxidized to the γ-nitro amides **6** with cerium ammonium nitrate. The configuration of the major diastereoisomer of **6**, obtained by column-chromatographic separation of the mixture, was determined by an X-ray crystal structure analysis.

In the crystal, both (*R*,*R*,*S*) and (*S*,*S*,*R*) enantiomers of **6** are present, each in two different conformations (molecules A and B) due to rotation about the C8−C9 bond. Views of the (*R*,*R*,*S*) enantiomers of molecules A and B are shown in Figures 1 and 2, respectively. Comparison of the ^{1}H-NMR spectra of **4a** and **4b** indicates that the major diastereoisomer has the same configuration in both cases. At present, this observation cannot be extended to products **4c** and **4d** merely on the basis of the simple analysis of ^{1}H-NMR spectra.

Figure 1. ORTEP view of the structure of the (*R*,*R*,*S*) enantiomer of molecule A together with the atom numbering scheme; the ellipsoids are drawn at a 30% probability level

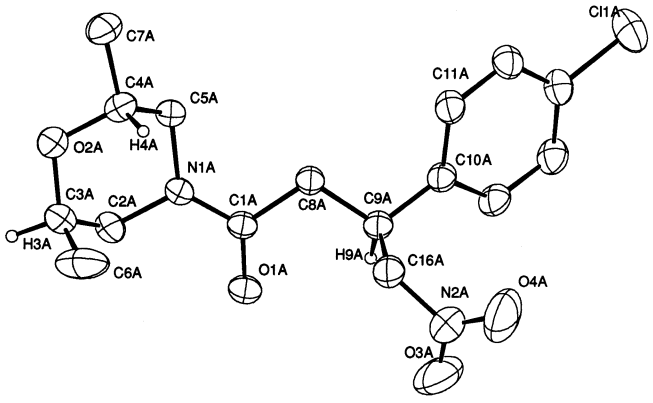
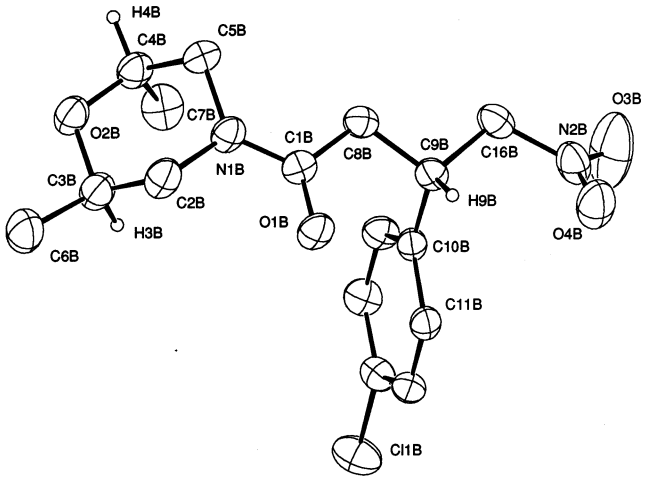
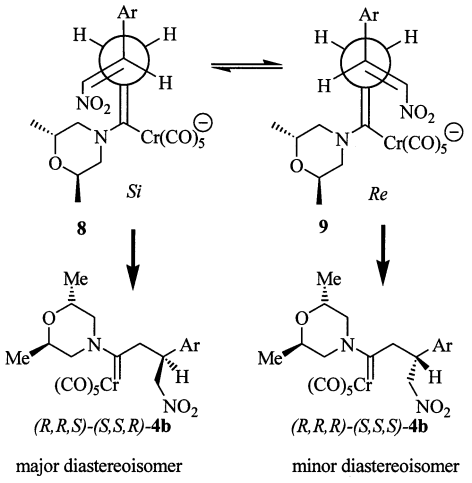


Figure 2. ORTEP view of the structure of the (*R,R,S*) enantiomer of molecule B together with the atom numbering scheme; the ellipsoids are drawn at a 30% probability level

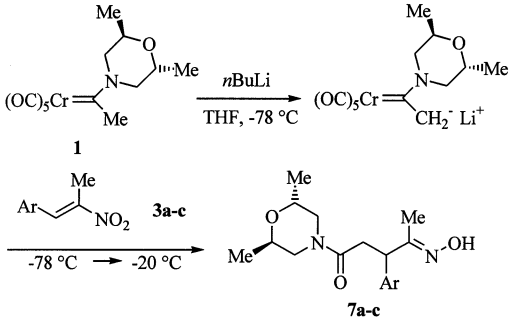


The stereochemical course of the reactions shown in Scheme 1 can be explained by considering models **8** and **9**, in analogy to the proposals of Seebach[12c] for the addition of enamines to nitrostyrenes, and more recently utilized by Mulzer[12d] in the case of the addition of an imide enolate to nitrostyrenes. Model **8**, in which the NO_2 group and the amine function are close together, is the favored one, leading to the (*R,R,S*)/(*S,S,R*)-**4b** diastereoisomer.



The second type of nitroalkenes examined were compounds **3a–c**; as above, the "metal enolate" of **1** was allowed to react with the appropriate Michael acceptor (Scheme 2, see General Procedure B). Surprisingly, in these cases, the isolated products were not organometallic but organic compounds, namely the hydroximo amides **7a–c**; chemical yields and diastereoselectivities are reported in Scheme 2. In compounds **7a–c** an oxygen atom is present in place of the pentacarbonylchromium group and an oxime function is in the place of the nitro group. It can be ruled out that the amide function arises from classical oxidation of amino carbenes into amides; in fact, such a reaction would also generate Cr^{III} salts (which were never observed) and, in any case, would require longer reaction times and the presence of an oxidant (see, for example, the conditions required for the oxidation of complex **4b** into **6**). In addition, the nitro groups of nitroalkenes and γ-nitro carbene complexes **4a–d** are not able to oxidize Cr^0 to Cr^{III}, as shown by the stability of the corresponding Michael adducts. We therefore assumed that the pentacarbonylchromium fragment may have been lost as Cr^0. To verify this hypothesis, we performed the reactions of complex **1** with the nitroalkenes **3a–c** in the presence of one equivalent of pyridine, which is a good donor ligand capable of acting as a trapping ligand for Cr^0. In all three cases, besides the hydroximo amides **7a–c**, isolated in the same chemical yields and with the same diastereoselectivities as those reported in Scheme 2, we isolated the adduct $PyCr(CO)_5$ in about 90% yield. As yet, we have been unable to separate the diastereoisomers of compounds **7** and so their configuration is still unknown, even though one might expect the same stereochemistry as found in products **4a**, **b**, and **6**.

Scheme 2



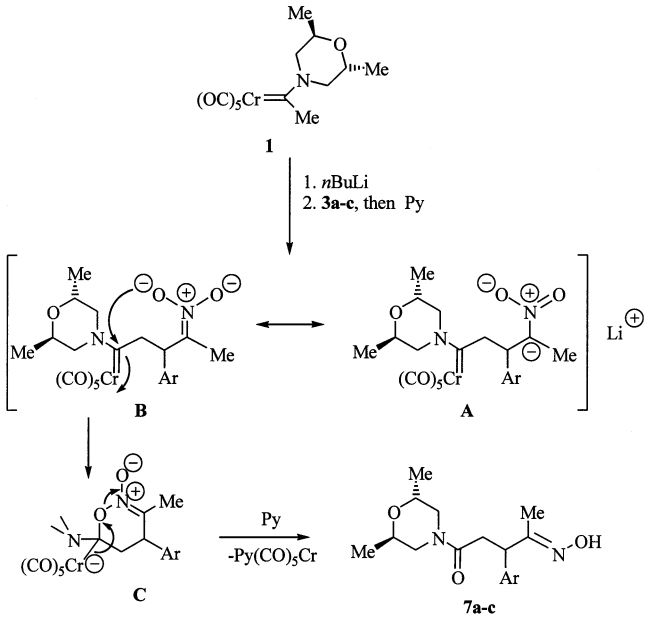
Entry	product	Ar	yield%	d.e.%
1	**7a**	Ph	80	30
2	**7b**	2-furyl	85	52
3	**7c**	2-thienyl	70	27

Finally, the geometry of the oximes **7a–c** can be assigned as (*E*), as indicated by an NOE between the methyl group and the hydrogen atom of the oxime function in the ^{1}H-NMR spectrum of compound **7b**.

On the basis of the aforementioned experimental and spectroscopic data, we propose a mechanism to account for the above reactions (Scheme 3).

Given the presence of the methyl substituent attached to the carbon atom bearing the nitro group, the initially formed 1,4-addition product is better described as nitronate anion **B** rather than tertiary carbanion **A**; nucleophilic attack of the oxy anion on the electrophilic carbene carbon atom can therefore take place, leading to the six-membered ring (structure **C**); the breaking of the oxygen–nitrogen and chromium–carbon bonds (as formally indicated in structure **C**) gives rise to the (*E*)-hydroximo amides **7**, plus the "$Cr(CO)_5$" species, which is trapped with pyridine to give the $PyCr(CO)_5$ complex[13].

Scheme 3



In conclusion, the first Michael addition of a "metal enolate" of a chiral Fischer-type amino carbene complex to conjugated nitroalkenes has been reported. Diastereoselectivities are higher than those obtained with the isolobal amide **5** or those reported in the literature in the case of the Li enolate of *N*,*N*-dimethylacetamide in the presence of chiral bases[12a].

Further studies on the scope of these reactions are in progress with the aim of delineating the factors influencing the diastereoselectivities, such as the use of different C_2-symmetric amines[3] or other chiral auxiliaries.

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Experimental Section

General: All reactions were carried out under nitrogen and the solvents were dried by distillation from sodium wire. Morpholino-substituted carbenechromium complex **1** was prepared as reported previously. Butyllithium solutions were titrated prior to use. Flash and vacuum chromatography was performed with Merck silica gel 60, 230−400 mesh. Diastereomeric excess (d.e.) values were calculated from the ^{1}H- or ^{13}C-NMR spectra of the crude reaction mixtures. The products **7a−c** were isolated as diastereoisomeric mixtures and upon injection into a GC/MS instrument gave two separated peaks with the same mass fragmentation. − IR: Perkin-Elmer FT-IR 1725 X. − ^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$): Bruker AC 300. − MS (EI, FAB): VG Analytical 7070 EQ. − GC-MS: MS Varian Saturn 3, GC Varian Star 3400 CX.

Synthesis of Complexes **4a−d**. − *General Procedure A:* In a three-necked flask equipped with an alcohol thermometer, the morpholino-substituted carbenechromium complex **1** (1 mmol, 0.333 g) was dissolved in anhydrous THF (48.7 ml, 2.05×10^{-2} M solution). The solution was cooled to −78°C under magnetic stirring. A hexane solution of *n*-butyllithium (1 mmol) was then added dropwise and allowed to react for 30 min at −78°C. Subsequently, a precooled solution of the appropriate nitroalkene **2a−d** (1 mmol) in THF (6 ml) was added over a period of 20 min and the mixture was allowed to react for a further 30 min or until all of the nitroalkene had been consumed. Then, a saturated ammonium chloride solution was added and the reaction vessel was allowed to warm to room temperature. The THF was evaporated in vacuo and the residue was extracted with dichloromethane (3 × 20 ml). The combined extracts were dried with Na_2SO_4 and filtered through a Celite pad. After removal of the solvent under reduced pressure, column chromatography (light petroleum/dichloromethane or light petroleum/ethyl acetate mixtures as eluents) afforded products **4a−d**.

Compound **4a**: Chromatographic separation gave 0.030 g (9%) of **1** and 0.414 g (86% total yield of the two diastereoisomers) of **4a** as a yellow, sticky oil; 30% d.e. The two diastereoisomers were separated by flash column chromatography and fully characterized.

4a (major diastereoisomer): Yellow solid, m.p. 90°C dec. (diethyl ether/pentane). − IR (Nujol): $\tilde{\nu}$ = 2052 (CO *trans*), 1907 (CO *cis*), 1556, 1379 (NO_2) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 1.10 (d, ^3J = 6.4 Hz, 3 H, CH_{3ax}), 1.27 (d, J = 6.4 Hz, 3 H, CH_{3eq}), 3.08 (dd, ^2J = 13.0 Hz, ^3J = 6.2 Hz, 1 H, NCHH_{ax}), 3.40 (dd, ^2J = 13.1 Hz, ^3J = 5.2 Hz, 1 H, Cr=CC*H*H), 3.60 (dd, ^2J = 13.1 Hz, ^3J = 9.9 Hz, 1 H, Cr=CCH*H*), 3.74 (dd, ^2J = 13.0 Hz, ^3J = 3.2 Hz, 1 H, NCH_{eq}H), 3.86−3.99 (m, 1 H, PhC*H*, superimposed by dd, ^2J = 13.1 Hz, ^3J = 7.7 Hz, 1 H, NCHH_{ax}), 4.10 (m, 1 H, CH_{3eq}C*H*O), 4.20 (m, 1 H, CH_{3ax}C*H*O), 4.37 (dd, ^2J = 13.2 Hz, ^3J = 2.7 Hz, 1 H, NCHH_{eq}), 4.77 (d, J = 7.6 Hz, 2 H, CH_2NO_2), 7.10−7.20 (m, 2 H, H arom.), 7.30−7.40 (m, 3 H, H arom.). − ^{13}C NMR ($CDCl_3$): δ = 17.1 (CH_{3ax}), 17.4 (CH_{3eq}), 41.8 (PhCH), 54.1 (*C*H$_2$C=Cr), 57.7 (NCH_2), 66.0 (NCH_2), 66.8 (CH_3*C*HO), 67.3 (CH_3*C*HO), 78.6 (CH_2NO_2), 127.4, 128.6, 129.4 (CH arom.), 137.0 (C_q arom.), 217.5 (CO *cis*), 222.4 (CO *trans*), 278.0 (C=Cr). − MS (FAB$^+$); *m/z*: 482 (10) [M$^+$], 454 (11) [M$^+$ − CO], 398 (43) [M$^+$ − 3 CO], 370 (54) [M$^+$ − 4 CO], 342 (10) [M$^+$ − 5 CO], 324 (50) [M$^+$ − 4 CO − NO_2], 306 (50), 290 (40) [M$^+$ −Cr(CO)$_5$], 256 (100). − $C_{21}H_{22}CrN_2O_8$ (482.42): calcd. C 52.28, H 4.60, N 5.80; found C 52.00, H 5.00, N 5.90.

4a (minor diastereoisomer): M.p. 89°C dec. (diethyl ether/pentane). − ^{1}H NMR ($CDCl_3$): δ = 1.02 (d, J = 6.4 Hz, 3 H, CH_{3ax}), 1.20 (d, J = 6.4 Hz, 3 H, CH_{3eq}), 2.85 (dd, ^2J = 13.1 Hz, ^3J = 3.4 Hz, 1 H, NCHH_{ax}), 3.18 (dd, ^2J = 12.7 Hz, ^3J = 9.1 Hz, 1 H, Cr=CC*H*H), 3.28 (dd, ^2J = 13.1 Hz, ^3J = 3.3 Hz, 1 H, NCH_{eq}H), 3.55−3.68 (m, 1 H, PhC*H*, superimposed by dd, ^2J = 13.0 Hz, ^3J = 8.1 Hz, 1 H, NCHH_{ax}), 3.74 (dd, ^2J = 12.7 Hz, ^3J = 5.2 Hz, 1 H, Cr=CCH*H*), 3.88 (m, 1 H, CH_{3eq}C*H*O), 4.20 (m, 1 H, CH_{3ax}C*H*O), 4.50 (br. d, ^2J = 13.2 Hz, 1 H, NCHH_{eq}), 4.80−4.95 (m, AB part of ABX system, 2 H, CH_2NO_2), 7.10−7.20 (m, 2 H, H arom.), 7.30−7.40 (m, 3 H, H arom.). − ^{13}C NMR ($CDCl_3$): δ = 16.4 (CH_{3ax}), 17.3 (CH_{3eq}), 42.4 (PhCH), 53.4 (*C*H$_2$C=Cr), 57.4 (NCH_2), 66.8 (CH_3*C*HO), 67.0 (NCH_2), 67.3 (CH_3*C*HO), 78.6 (CH_2NO_2), 127.6, 128.6, 129.4 (CH arom.), 137.2 (C_q arom.), 217.5 (CO *cis*), 222.2 (CO *trans*), 274.1 (C=Cr).

Compound **4b**: Chromatographic separation gave 0.053 g (16%) of **1** and 0.413 g (80% total yield of the two diastereoisomers) of **4b** as a yellow, sticky oil; m.p. (pentane/diethyl ether) 55°C (mixture

of diastereoisomers); 50% d.e. The two diastereoisomers were separated and fully characterized.

4b (major diastereoisomer): Yellow solid, m.p. 100−102°C dec. (diethyl ether/pentane). − IR (Nujol): $\tilde{\nu}$ = 2053 (CO *trans*), 1908 (CO *cis*), 1556, 1378 (NO_2) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.16 (d, *J* = 6.5 Hz, 3 H, CH_{3ax}), 1.28 (d, *J* = 6.4 Hz, 3 H, CH_{3eq}), 3.38 (dd, ^2J = 13.5 Hz, ^3J = 5.8 Hz, 1 H, Cr=CC*H*H, superimposed by dd, 1 H, ^2J = 12.8 Hz, ^3J = 5.5 Hz, NCHH_{ax}), 3.63 (dd, ^2J = 13.5 Hz, ^3J = 9.5 Hz, 1 H, Cr=CC*H*H), 3.78 (dd, ^2J = 12.8 Hz, ^3J = 3.4 Hz, 1 H, NCH_{eq}H), 3.88 (m, 1 H, *p*-ClPhC*H*, superimposed by dd, ^2J = 13.3 Hz, ^3J = 8.6 Hz, 1 H, NCHH_{ax}), 4.15 (m, 1 H, CH_{3ax}C*H*O), 4.23 (m, 1 H, CH_{3eq}C*H*O), 4.46 (dd, ^2J = 13.3 Hz, ^3J = 2.6 Hz, 1 H, NCH_{eq}H), 4.70 (d, *J* = 7.6 Hz, 2 H, CH_2NO_2), 7.09 (d, ^3J = 8.4 Hz, 2 H, H arom.), 7.33 (d, ^3J = 8.4 Hz, 2 H, H arom.). − ^{13}C NMR ($CDCl_3$): δ = 16.9 (CH_{3ax}), 17.6 (CH_{3eq}), 41.3 (*p*-ClPh*C*H) 53.9 (*C*H_2C=Cr), 58.0 (NCH_2), 66.5 (NCH_2), 67.1 (CH_3*C*HO), 67.3 (CH_3*C*HO), 78.5 (CH_2NO_2), 128.8, 129.6 (CH arom.), 134.6 (C_q arom.), 135.9 (C_q arom.), 217.4 (CO *cis*), 222.3 (CO *trans*), 278.7 (C=Cr). − MS (FAB$^+$); *m/z*: 516 (10) [M^+], 488 (10) [M^+ − CO], 432 (35) [M^+ − 3 CO], 404 (50) [M^+ − 4 CO], 376 (10) [M^+ − 5 CO], 358 (50) [M^+ − 4 CO − NO_2], 341 (40), 325 (45) [M^+ − $Cr(CO)_5$], 291 (100). − $C_{21}H_{21}ClCrN_2O_8$ (516.85): calcd. C 48.80, H 4.10, N 5.42; found C 47.9, H 4.08, N 5.59.

4b (minor diastereoisomer): Yellow solid, m.p. 88−90°C dec. (diethyl ether/pentane). − ^1H NMR ($CDCl_3$): δ = 1.09 (d, *J* = 6.5 Hz, 3 H, CH_{3ax}), 1.22 (d, *J* = 6.6 Hz, 3 H, CH_{3eq}), 2.98 (dd, ^2J = 13.0 Hz, ^3J = 3.3 Hz, 1 H, NCHH_{ax}), 3.12 (dd, ^2J = 12.7 Hz, ^3J = 8.5 Hz, 1 H, Cr=CC*H*H), 3.36 (br. dd, ^2J = 13.0 Hz, ^3J = 4.2 Hz, 1 H, NCH_{eq}H), 3.64 (dd, ^2J = 13.0 Hz, ^3J = 8.2 Hz, 1 H, NCHH_{ax}), 3.70−3.82 (m, 1 H, CH_{3ax}C*H*O, superimposed by dd, ^2J = 12.7 Hz, ^3J = 5.9 Hz, 1 H, Cr=CCH*H*), 3.83 (m, 1 H, *p*-ClPhC*H*), 4.2 (m, 1 H, CH_{3eq}C*H*O), 4.54 (br. d, ^2J = 13.0 Hz, 1 H, NCHH_{eq}), 4.76−4.90 (m, AB part of ABX system, 2 H, CH_2NO_2), 7.11 (d, ^3J = 8.4 Hz, 2 H, H arom.), 7.34 (d, ^3J = 8.4 Hz, 2 H, H arom.). − ^{13}C NMR ($CDCl_3$): δ = 16.4 (CH_{3ax}), 17.4 (CH_{3eq}), 42.0 (*p*-ClPh*C*H), 53.4 (*C*H_2C=Cr), 57.7 (NCH_2), 66.8 (CH_3*C*HO), 67.2 (NCH_2), 67.5 (CH_3*C*HO), 78.5 (CH_2NO_2), 128.9, 129.7 (CH arom.), 134.6 (C_q arom.), 135.9 (C_q arom.), 217.4 (CO *cis*), 222.1 (CO *trans*), 274.7 (C=Cr).

Compound **4c**: Chromatographic separation gave 0.023 g (7%) of **1** and 0.415 g (91% total yield of the two diastereoisomers) of **4c** as a yellow, sticky oil; m.p. (pentane/diethyl ether) 91−92°C (4:1 mixture of diastereoisomers); 40%d.e. The two diastereoisomers were separated and fully characterized.

4c (major diastereoisomer): Yellow solid, m.p. 102−104°C dec. (diethyl ether/pentane). − IR (Nujol): $\tilde{\nu}$ = 2055 (CO *trans*), 1903 (CO *cis*), 1562, 1382 (NO_2) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.12 (d, *J* = 6.4 Hz, 3 H, CH_{3ax}), 1.20 (d, *J* = 6.4 Hz, 3 H, CH_{3eq}), 2.95 (dd, ^2J = 13.2 Hz, ^3J = 3.6 Hz, 1 H, NCHH_{ax}), 3.29 (dd, ^2J = 12.3 Hz, ^3J = 10.8 Hz, 1 H, Cr=CC*H*H), 3.46 (ddd, ^2J = 13.2 Hz, ^3J = 3.7 Hz, ^4J = 2.0 Hz, 1 H, NCH_{eq}H), 3.54−3.64 (m, 2 H, Cr=CCH*H* + NCHH_{ax}), 3.82 (m, 1 H, Fur-C*H*), 4.10 (m, 1 H, CH_{3ax}C*H*O), 4.17 (m, 1 H, CH_{3eq}C*H*O), 4.59 (ddd, ^2J = 13.0 Hz, ^3J = ^4J = 2.0 Hz, 1 H, NCHH_{eq}), 4.73 (dd, A part of an ABX system, 1 H, C*H*HNO_2), 4.86 (dd, B part of an ABX system, 1 H, CH*H*NO_2), 6.12 (m, 1 H, Fur-H), 6.35 (m, 1 H, Fur-H), 7.35 (m, 1 H, Fur-H). − ^{13}C NMR ($CDCl_3$): δ = 16.2 (CH_{3ax}), 17.5 (CH_{3eq}), 35.6 (Fur-*C*H), 50.8 (*C*H_2C=Cr), 56.4 (NCH_2), 66.7 (CH_3*C*HO), 67.3 (NCH_2), 67.7 (CH_3*C*HO), 76.7 (CH_2NO_2), 109.6, 111.4, 142.9 (Fur-CH), 149.6 (Fur-C_q), 217.6 (CO *cis*), 222.4 (CO *trans*), 271.9 (C=Cr). − MS (FAB$^+$); *m/z*: 472 (10) [M^+], 444 (8) [M^+ − CO], 360 (45) [M^+ − 4 CO], 332 (70) [M^+ − 5 CO], 281 (40) [M^+ − $Cr(CO)_5$ + 1], 249 (30) [M^+ − $Cr(CO)_5$ − HNO], 247 (100), 234 (30) [M^+ − $Cr(CO)_5$ − HNO_2]. − $C_{19}H_{20}CrN_2O_9$ (472.35): calcd. C 48.31, H 4.27, N 5.93; found C 48.56, H 4.70, N 5.98.

4c (minor diastereoisomer): Yellow gummy solid. − ^1H NMR ($CDCl_3$): δ = 1.16 (d, *J* = 6.4 Hz, 3 H, CH_{3ax}), 1.32 (d, *J* = 6.4 Hz, 3 H, CH_{3eq}), 3.1 (dd, ^2J = 13.10 Hz, ^3J = 6.9 Hz, 1 H, NCHH_{ax}), 3.28 (dd, ^2J = 13.0 Hz, ^3J = 4.6 Hz, 1 H, Cr=CC*H*H), 3.71 (dd, ^2J = 13.0 Hz, ^3J = 11.1 Hz, 1 H, Cr=CCH*H*), 3.86 (dd, ^2J = 13.1 Hz, ^3J = 3.0 Hz, 1 H, NCH_{eq}H), 4.00 (m, 1 H, Fur-C*H*), 4.10 (m, 2 H, CH_{3ax}C*H*O + NCHH_{ax}), 4.27 (m, 1 H, CH_{3eq}C*H*O), 4.35 (dd, ^2J = 13.0 Hz, ^3J = 3.0 Hz, 1 H, NCHH_{eq}), 4.63−4.82 (ddd, AB part of ABX system, 2 H, CH_2NO_2), 6.12 (m, 1 H, Fur-H), 6.35 (m, 1 H, Fur-H), 7.35 (m, 1 H, Fur-H). − ^{13}C NMR ($CDCl_3$): δ = 17.2 (CH_{3ax}), 17.3 (CH_{3eq}), 35.3 (Fur-*C*H), 52.0 (*C*H_2C=Cr), 57.4 (NCH_2), 65.8 (NCH_2), 66.6 (CH_3*C*HO), 67.7 (CH_3*C*HO), 77.0 (CH_2NO_2), 108.4, 111.1, 142.7 (Fur-CH), 149.4 (Fur-C_q), 217.4 (CO *cis*), 222.6 (CO *trans*), 276.8 (C=Cr).

Compound **4d**: Chromatographic separation gave 0.020 g (6%) of **1** and 0.444 g (91% yield) of **4d** as a yellow solid (mixture of the two diastereoisomers); m.p 92−95°C (pentane/diethyl ether); 20% d.e. The two diastereoisomers were separated and fully characterized.

4d (major diastereoisomer): Yellow solid, m.p. 101−103°C dec. (diethyl ether/pentane). − IR (Nujol): $\tilde{\nu}$ = 2052 (CO *trans*), 1907 (CO *cis*), 1556, 1378 (NO_2) cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.09 (d, *J* = 6.4 Hz, 3 H, CH_{3ax}), 1.22 (d, *J* = 6.4 Hz, 3 H, CH_{3eq}), 3.02 (dd, ^2J = 13.1 Hz, ^3J = 3.4 Hz, 1 H, NCHH_{ax}), 3.24 (dd, ^2J = 12.7 Hz, ^3J = 9.4 Hz, 1 H, Cr=CC*H*H), 3.45 (br. dd, ^2J = 13.1 Hz, ^3J = 4.1 Hz, 1 H, NCH_{eq}H), 3.67 (dd, ^2J = 12.7 Hz, ^3J = 8.3 Hz, 1 H, NCHH_{ax}), 3.76 (m, 2 H, CH_{3ax}C*H*O + Cr=CCH*H*), 4.22 (m, 2 H, thienyl-C*H* + CH_{3eq}C*H*O), 4.58 (br. d, *J* = 13.0 Hz, 1 H, NCH_{eq}H), 4.75−4.90 (AB part of an ABX system, 2 H, CH_2NO_2), 6.90 (m, 1 H, thienyl-H), 6.95 (m, 1 H, thienyl-H), 7.25 (m, 1 H, thienyl-H). − ^{13}C NMR ($CDCl_3$): δ = 16.5 (CH_{3ax}), 17.5 (CH_{3eq}), 37.6 (thienyl-*C*H), 54.1 (*C*H_2C=Cr), 57.2 (NCH_2), 66.9 (CH_3*C*HO), 67.2 (NCH_2), 67.6 (CH_3*C*HO), 79.5 (CH_2NO_2), 125.8, 126.4, 127.6 (thienyl-CH), 139.1 (thienyl-C_q), 217.4 (CO *cis*), 222.2 (CO *trans*), 273.6 (C=Cr). − MS (FAB$^+$): *m/z* = 488 (9) [M^+], 460 (20) [M^+ − CO], 404 (65) [M^+ − 3 CO], 376 (20) [M^+ − 4 CO], 348 (30) [M^+ − 5 CO], 330 (25) [M^+ − 4 CO − NO_2], 297 (40) [M^+ − $Cr(CO)_5$ + 1], 265 (50) [M^+ − $Cr(CO)_5$ − HNO], 263 (100), 250 (20) [M^+ − $Cr(CO)_5$ − HNO_2]. − $C_{19}H_{20}CrN_2O_8S$ (488.43): calcd. C 46.72, H 4.13, N 5.73; found C 46.73, H 4.19, N 5.50.

4d (minor diastereoisomer): Yellow solid, m.p. 91−93°C dec. (diethyl ether/pentane). − ^1H NMR ($CDCl_3$): δ = 1.14 (d, *J* = 6.4 Hz, 3 H, CH_{3ax}), 1.30 (d, *J* = 6.4 Hz, 3 H, CH_{3eq}), 3.20 (dd, ^2J = 13.0 Hz, ^3J = 6.1 Hz, 1 H, NCHH_{ax}), 3.38 (dd, ^2J = 13.2 Hz, ^3J = 5.4 Hz, 1 H, Cr=CC*H*H), 3.67 (dd, ^2J = 13.2 Hz, ^3J = 10.0 Hz, 1 H, Cr=CCH*H*), 3.82 (dd, ^2J = 13.0 Hz, ^3J = 3.2 Hz, 1 H, NCH_{eq}H), 3.98 (dd, ^2J = 13.2 Hz, ^3J = 7.7 Hz, 1 H, NCHH_{ax}), 4.13 (m, 1 H, CH_{3ax}C*H*O), 4.25 (m, 2 H, thienyl-C*H* + CH_{3eq}C*H*O), 4.43 (dd, ^2J = 13.2 Hz, ^3J = 2.9 Hz, 1 H, NCHH_{eq}), 4.77 (d, ^2J = 7.4 Hz, 2 H, CH_2NO_2), 6.90 (m, 1 H, thienyl-H), 6.95 (m, 2 H, thienyl-H). − ^{13}C NMR ($CDCl_3$): δ = 17.2 (CH_{3ax}), 17.4 (CH_{3eq}), 36.8 (thienyl-*C*H), 54.4 (*C*H_2C=Cr), 57.7 (NCH_2), 66.2 (NCH_2), 66.8 (CH_3*C*HO), 67.4 (CH_3*C*HO), 79.1 (CH_2NO_2), 125.3, 126.4, 127.6 (thienyl-CH), 140.2 (thienyl-C_q), 217.5 (CO *cis*), 222.3 (CO *trans*), 277.6 (C=Cr).

Synthesis of Compounds **7a−c**. − *General Procedure B:* In a three-necked flask equipped with an alcohol thermometer, mor-

pholino-substituted carbenechromium complex **1** (1 mmol, 0.333 g) was dissolved in anhydrous THF (10 ml, solution 10^{-1} M) under nitrogen. The solution was cooled to −78°C under magnetic stirring. A hexane solution of *n*-butyllithium (1 mmol) was then added dropwise and allowed to react for 30 min at −78°C. Subsequently, a solution of the appropriate nitroalkene **3a−c** (1.3 mmol) in THF (7 ml) was added over a period of 50 min and the reaction mixture was allowed to react for a further 20 min. Then, MeOH[15] was added at −78°C and the mixture was allowed to warm to room temperature. The THF was evaporated in vacuo, and the residue was treated with a saturated solution of sodium chloride and extracted with diethyl ether (3 × 20 ml). The organic phase was dried with Na_2SO_4, filtered through a Celite pad, and the solvent was evaporated. The corresponding products **7a−c** were isolated, besides small amounts of **1**, after column chromatography (eluent: diethyl ether/dichloromethane/light petroleum, 3:1:1). − *General Procedure C:* The procedure was identical to procedure B except that dry pyridine (1 mmol) was added before the appropriate nitroalkene.

Compound **7a**: According to General Procedure B. Chromatographic separation gave 0.055 g (17%) of **1** and 0.243 g (80%) of **7a** as a mixture of diastereoisomers; 30% d.e. − According to General Procedure C. Chromatographic separation gave 0.238 g (88%) of $PyCr(CO)_5$, 0.040 g (12%) of **1** and 0.240 g (79%) of **7a** as a mixture of diastereoisomers; 30% d.e.

7a: White solid, m.p. 117−118°C (*n*-pentane/diethyl ether). − IR (Nujol): $\tilde{\nu}$ = 3336.8 (OH), 1623.6 (N−CO) cm^{-1}. − ^{1}H NMR: δ = 1.07 (d, ^3J = 6.6 Hz, CH_{3ax}), 1.15 (d, ^3J = 6.4 Hz, 3 H, $CH_{3eq.}$), 1.75 (s, 3 H, C*H*$_3$C=NOH), 2.45 (dd, ^2J = 15.6 Hz, ^3J = 5.7 Hz, 1 H, O=CCH*H*), 3.05 (dd, ^2J = 13.3 Hz, ^3J = 6.4 Hz, 1 H, NCH*H*), 3.14 (dd, ^2J = 15.6 Hz, ^3J = 8.7 Hz, 1 H, O=CC*H*H), 3.27 (dd, ^2J = 13.2 Hz, ^3J = 6.6 Hz, 1 H, NC*H*H), 3.51 (dd, ^2J = 13.2 Hz, ^3J = 3.3 Hz, 1 H, NC*H*H), 3.66 (dd, ^2J = 13.2 Hz, ^3J = 3.4 Hz, 1 H, NCH*H*), 3.92 (m, 2 H, CH$_3$C*H*O), 4.13 (m, 1 H, PhC*H*), 7.15 (s, 1 H, =NO*H*), 7.20−7.35 (m, 5 H, H arom.). − ^{13}C NMR: δ = 14.4 (*C*H$_3$C=NOH), 17.2 (CH_{3ax}), 17.5 (CH_{3eq}), 36.4 (*C*H$_2$C=O), 46.5 (NCH_2), 48.1 (Ph*C*H), 50.4 (NCH_2), 65.8 (CH$_3$*C*HO), 66.3 (CH$_3$*C*HO), 127.2−128.8 (CH arom.), 140.6 (C_q arom.), 158.7 (C=NOH), 170.0 (NCO). − MS (EI, 70 eV): *m/z* (%): 304 (15) [M^+], 287 (45), 247 (35), 190 (100), 116 (85). − $C_{17}H_{24}N_2O_3$ (304.38): calcd. C 67.08, H 7.95, N 9.20; found C 67.02, H 7.84, N 9.15.

Compound **7b**: According to General Procedure B. Chromatographic separation gave 0.025 g (7.5%) of **1** and 0.250 g (85%) of **7b** as a mixture of diastereoisomers; 52% d.e. − According to General Procedure C. Chromatographic separation gave 0.243 g (90%) of $PyCr(CO)_5$, 0.023 g (7%) of **1** and 0.235 g (80%) of **7b** as a mixture of diastereoisomers; 53% d.e.

7b: White solid, m.p. 101−103°C (*n*-pentane). − IR (Nujol): $\tilde{\nu}$ = 3352 (OH), 1631 (N−CO) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 1.10 (d, ^3J = 6.5 Hz, 3 H, $CH_{3ax.}$), 1.18 (d, ^3J = 6.5 Hz, 3 H, $CH_{3eq.}$), 1.80 (s, 3 H, C*H*$_3$C=NOH), 2.77 (dd, ^2J = 15.3 Hz, ^3J = 6.7 Hz, 1 H, O=CCH*H*), 3.02 (dd, ^2J = 15.4 Hz, ^3J = 7.8 Hz, 1 H, O=CC*H*H), 3.14 (dd, ^2J = 13.1 Hz, ^3J = 6.7 Hz, 1 H, NC*H*H), 3.30 (dd, ^2J = 13.1 Hz, ^3J = 6 Hz, 1 H, NCH*H*), 3.45 (dd, ^2J = 13.1 Hz, ^3J = 3 Hz, 1 H, NC*H*H), 3.63 (dd, ^2J = 13.3 Hz, ^3J = 3 Hz, 1 H, NCH*H*), 3.96 (m, 2 H, CH$_3$C*H*O), 4.22 (m, 1 H, Fur-C*H*), 6.10 (d, *J* = 3.0 Hz, 1 H, Fur-H), 6.30 (d, *J* = 2.3 Hz, 1 H, Fur-H), 7.30 (d, *J* = 1.5 Hz, 1 H, Fur-H), 7.45 (s, 1 H, NO*H*). − ^{13}C NMR ($CDCl_3$): δ = 13.4 (*C*H$_3$C=NOH), 17.2 ($CH_{3ax.}$), 17.5 (CH_{3eq}), 33.7 (CO*C*H$_2$), 41.6 (Fur-*C*H), 46.6 (NCH_2), 50.7 (NCH_2), 65.7 (CH$_3$*C*HO), 66.5 (CH$_3$*C*HO), 107.2, 110.5 (Fur-CH), 142.0 (Fur-CHO), 153.4 (Fur-C_q), 156.8 (C=NOH), 169.8 (NCO). − MS (EI); *m/z* (%): 294 (50) [M^+], 277 (100), 179 (100), 162 (100), 116 (100). − $C_{15}H_{22}N_2O_4$ (294.34): calcd. C 61.21, H 7.53, N 9.51; found C 62.21, H 7.47, N 9.51.

Compound **7c**: According to General Procedure B. Chromatographic separation gave 0.057 g (17%) of **1** and 0.217 g (70%) of **7c** as a mixture of diastereoisomers; 27% d.e. − According to General Procedure C. Chromatographic separation gave 0.233 g (86%) of $PyCr(CO)_5$, 0.054 g (16%) of **1** and 0.230 g (74%) of **7c** as a mixture of diastereoisomers; 27% d.e.

7c: White solid, m.p. 136−137°C (*n*-pentane/diethyl ether). − IR (Nujol): $\tilde{\nu}$ = 3327 (N−OH), 1634 (N−CO) cm^{-1}. − ^{1}H NMR: δ = 1.08 (d, ^3J = 6.4 Hz, 3 H, $CH_{3ax.}$), 1.17 (d, ^3J = 6.4 Hz, 3 H, $CH_{3eq.}$), 1.85 (s, 3 H, C*H*$_3$C=NOH), 2.70 (dd, ^2J = 15.4 Hz, ^3J = 6.6 Hz, 1 H, O=CC*H*H), 3.08 (dd, ^2J = 15.3 Hz, ^3J = 7.1 Hz, 1 H, O=CCH*H*), 3.10 (dd, ^2J = 13 Hz, ^3J = 6.4 Hz, 1 H, NCH*H*), 3.30 (dd, ^2J = 12.9 Hz, ^3J = 6.0 Hz, 1 H, NCH*H*), 3.40 (dd, ^2J = 13.3 Hz, ^3J = 3.1 Hz, 1 H, NC*H*H), 3.60 (dd, ^2J = 13.3 Hz, ^3J = 3.7 Hz, 1 H, NC*H*H), 3.95 (m, 2 H, CH$_3$C*H*O), 4.40 (m, 1 H, thienyl-C*H*), 6.90 (m, 2 H, thienyl-H), 7.20 (m, 2 H, NOH + thienyl-H). − ^{13}C NMR: δ = 13.9 (*C*H$_3$C=NOH), 17.3 ($CH_{3ax.}$), 17.6 ($CH_{3eq.}$), 37.2 (*C*H$_2$CO), 43.2 (thienyl-*C*H), 46.3 (NCH_2), 50.7 (NCH_2), 65.7 (CH$_3$*C*HO), 66.6 (CH$_3$*C*HO), 124.7, 125.8, 126.9 (thienyl-CH), 144.0 (thienyl-C_q), 158.5 (C=NOH), 169.8 (NCO). − MS (EI): *m/z* (%): 310 (5) [M^+], 293 (65), 195 (100), 178 (100), 116 (85). − $C_{15}H_{22}N_2O_3S$ (310.40): calcd. C 58.04, H 7.14, N 9.02; found C 57.18, H 7.17, N 8.79.

Synthesis of Compound **5**: 2,6-*trans*-Dimethylmorpholine (10 mmol, 1.15 g) was acetylated according to a standard procedure to yield 1.52 g (94%) of **5**.

5: Pale-yellow oil. − IR (neat): $\tilde{\nu}$ = 1646, 1032 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 1.10 (d, ^3J = 6.5 Hz, 3 H, CH_{3ax}), 1.20 (d, ^3J = 6.5 Hz, 3 H, CH_{3eq}), 2.05 (s, 3 H, CH_3CO), 3.10 (dd, ^2J = 13.2 Hz, ^3J = 7.0 Hz, 1 H, NCHH_{ax}), 3.15 (dd, ^2J = 13.2 Hz, ^3J = 5.5 Hz, 1 H, NCHH_{ax}), 3.45 (dd, ^2J = 13.2 Hz, ^3J = 3.3 Hz, 1 H, NCH_{eq}H), 3.78 (dd, ^2J = 13.2 Hz, ^3J = 2.9 Hz, 1 H, NCH_{eq}H), 3.95 (m, 2 H, CH$_3$C*H*O). − ^{13}C NMR ($CDCl_3$): δ = 17.0 (CH_{3ax}), 17.4 (CH_{3eq}), 21.0 (*C*H$_3$CO), 45.7 (NCH_2), 50.6 (NCH_2), 65.3 (CH$_3$*C*HO), 167.9 (CO). − MS (70 eV): *m/z:* 157 (40) [M^+], 142 (50), 114 (25), 113 (100).

Synthesis of Compound **6**. − *Procedure D:* In a three-necked flask equipped with an alcohol thermometer, *N*-acetylmorpholine (**5**) (1 mmol, 0.1572 g) was dissolved in anhydrous THF (48.7 ml, 2.05 × 10^{-2} M solution). The solution was cooled to −78°C under magnetic stirring. A hexane solution of *n*-butyllithium (1 mmol) was added dropwise and allowed to react for 30 min at −78°C. Then, a precooled (−78°C) solution of the nitroalkene **2b** (1 mmol) in THF (6 ml) was added over a period of 20 min and the mixture was allowed to react for a further 30 min. Subsequently, a saturated ammonium chloride solution was added and the reaction vessel was allowed to warm to room temperature. The THF was evaporated in vacuo, the mixture was extracted with dichloromethane (3 × 20 ml), and the combined extracts were dried with Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography (eluent: light petroleum/diethyl ether/ethyl acetate, 1:1:1) affording product **6**, besides a minor amount of compound **5** (eluted with ethyl acetate/methanol, 1:1). Further chromatography gave 0.059 g (38%) of **5** and 0.170 g (50% total yield of the two diastereoisomers) of **6** as a colourless, sticky oil; 6% d.e. The two diastereoisomers were then separated by flash column chromatography and fully characterized. − The reaction was also performed using LDA as the base, prepared from freshly distilled diisopropylamine

and *n*-butyllithium at 0°C under dry and inert atmosphere. Chromatography gave 0.030 g (19%) of **5** and 0.263 g (77% total yield of the two diastereoisomers) of **6** as a colourless, sticky oil; 5% d.e.

6 (major diastereoisomer): White solid, m.p. 106−108°C (diisopropyl ether). − IR (film): $\tilde{\nu}$ = 1646, 1552, 1494, 1455, 1378 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.15 (d, *J* = 6.4 Hz, 6 H, 2 CH_3), 2.66 (dd, part A of ABX, ^2J = 16.2 Hz, ^3J = 6.2 Hz, 1 H, O=CCH*H*), 2.77 (dd, part B of ABX, ^2J = 16.2 Hz, ^3J = 7.8 Hz, 1 H, O=CC*H*H), 3.09 (dd, ^2J = 13.1 Hz, ^3J = 5.9 Hz, 1 H, NCHH_{ax}), 3.18 (dd, ^2J = 13.2 Hz, ^3J = 6.7 Hz, 1 H, NCHH_{ax}), 3.42 (dd, ^2J = 13.1 Hz, ^3J = 3.6 Hz, 1 H, NCH_{eq}H), 3.70 (dd, ^2J = 13.2 Hz, ^3J = 3.4 Hz, 1 H, NCH_{eq}H), 3.90−4.00 (m, 2 H, CH_3C*H*O), 4.06 (m, 1 H, *p*-ClPhC*H*), 4.66 (dd, ^2J = 12.6 Hz, ^3J = 7.8 Hz, 1 H, CH*H*NO_2), 4.83 (dd, ^2J = 12.6 Hz, ^3J = 6.2 Hz, 1 H, C*H*HNO_2), 7.13 (m, 2 H, H arom.), 7.30 (m, 2 H, H arom.). − ^{13}C NMR ($CDCl_3$): δ = 17.2 (CH_{3ax}), 17.5 (CH_{3eq}), 35.7 (*C*H_2CO), 39.6 (*p*-ClPh*C*H), 46.6 (NCH_2), 50.3 (NCH_2), 65.8 (CH_3*C*HO), 66.0 (CH_3*C*HO), 79.3 (CH_2NO_2), 128.8, 129.2 (CH arom.), 133.7 (C_q arom.), 137.7 (ClC_q arom.), 168.3 (CO). − MS (70 eV); *m/z*: 341 (65) [M^+], 323 (15) [M^+ − 18], 294 (100) [M^+ − HNO_2], 250 (70), 179 (50). − $C_{16}H_{21}ClN_2O_4$ (340.8): calcd. C 56.40, H 6.20, N 8.17; found C 56.27, H 6.23, N 8.20.

6 (minor diastereoisomer): White solid, m.p. 75−77°C (diisopropyl ether). − ^1H NMR ($CDCl_3$): δ = 1.10 (d, *J* = 6.4 Hz, 3 H, CH_{3ax}), 1.18 (d, *J* = 6.4 Hz, 3 H, CH_{3eq}), 2.71 (m, 2 H, O=CCH_2), 3.09 (dd, ^2J = 13.1 Hz, ^3J = 6.3 Hz, 1 H, NCHH_{ax}), 3.20 (dd, ^2J = 13.3 Hz, ^3J = 6.4 Hz, 1 H, NCHH_{ax}), 3.41 (dd, ^2J = 13.1 Hz, ^3J = 3.5 Hz, 1 H, NCH_{eq}H), 3.67 (dd, ^2J = 13.4 Hz, ^3J = 3.5 Hz, 1 H, NCH_{eq}H), 3.80−4.00 (m, 2 H, CH_3C*H*O), 4.03 (m, 1 H, *p*-ClPhC*H*), 4.67 (dd, ^2J = 12.5 Hz, ^3J = 8.0 Hz, 1 H, CH*H*NO_2), 4.84 (dd, ^2J = 12.6 Hz, ^3J = 6.1 Hz, 1 H, C*H*HNO_2), 7.15 (m, 2 H, H arom.), 7.30 (m, 2 H, H arom.). − ^{13}C NMR ($CDCl_3$): δ = 17.3 (CH_{3ax} + CH_{3eq}), 35.8 (*C*H_2CO), 39.7 (*p*-ClPh*C*H), 46.5 (NCH_2), 50.5 (NCH_2), 65.7 (CH_3*C*HO), 66.2 (CH_3*C*HO), 79.3 (CH_2NO_2), 128.8, 129.2 (CH arom.), 133.8 (C_q arom.), 137.6 (ClC_q arom.), 168.3 (CO).

Oxidation of Compound **4b to 6**: To a solution of compound **4b** (0.516 g, 1 mmol) in acetone (40 ml), a solution of cerium ammonium nitrate CAN (3 mmol) in 10 ml of acetone was added dropwise at room temperature over a period of 2 h. Subsequently, the solvent was evaporated, the residue was extracted with dichloromethane, and the combined extracts were washed with brine and dried with sodium sulfate. Chromatography (eluent: petroleum ether/diethyl ether/ethyl acetate, 1:1:1) gave 0.305 g (90% yield) of **6**.

X-ray Crystal-Structure Determination of **6**: Crystal data: $C_{16}H_{21}ClN_2O_4$, M_r = 340.80, triclinic, space group $P\bar{1}$, *a* = 19.408(4), *b* = 10.660(5), *c* = 9.599(3) Å, α = 65.79(2), β = 91.27(3), γ = 78.09(2)°, *V* = 1759(1) $Å^3$, *Z* = 4, D_x = 1.287 g/cm^3, *F*(000) = 720, λ = 1.54184 Å, μ(Cu-K_α) = 2.104 mm^{-1}. Crystal dimensions: 0.21 × 0.15 × 0.27 mm. The intensity data were collected at room temperature (22°C) with an Enraf-Nonius CAD-4 single-crystal diffractometer using graphite-monochromated Cu-K_α radiation and the θ/2θ scan technique. Final unit-cell parameters were obtained from a least-squares refinement using 23 reflections. 6469 independent reflections were measured (with θ in the range 3−70°) and included in the structural refinement. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) with anisotropic thermal parameters in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding carbon atoms. In the final cycles of refinement, a weighting scheme $w = 1/[s^2F_o^2 + (0.1319\ P)^2]$, where $P = (F_o^2+2F_c^2)/3$ was used. The refinement converged at wR_2 = 0.2006 for all data and 423 variables [R_1 = 0.0552 for 4308 reflections with $I > 2\sigma(I)$]. The minimum and maximum peaks in the final difference Fourier map were −0.436 and 0.311 $eÅ^{-3}$. − All calculations were carried out with the CNRDIF computers of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, using the SHELXS-86 and SHELXL-92 crystallographic computer programs[16]. − Details of the crystal structure investigation have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101331. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U. K. [Fax: (internat.) + 44-1223/33603; E-mail: deposit@ccdc.cam.ac.uk].

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[3] In addition to complex **1**, another chiral carbene complex substituted with the C_2-symmetric *trans*-3,5-dimethylpiperidine has been synthesized in our laboratory, and the corresponding α-anion has been employed in the 1,4-addition reaction. Due to the absence of the six-membered ring flipping, these two complexes exist both in solution and in the solid state as a single, stable, conformationally rigid rotamer[4].

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